HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

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ENVIRONMENTS OF FERROMANGANESE CONCRETIONS IN THE NORTHERN GULF OF FINLAND

Anna Sippo
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UNIVERSITY OF HELSINKI
FACULTY OF SCIENCE
DEPARTMENT OF GEOSCIENCES AND GEOGRAPHY
DIVISION OF GEOLOGY

HELSINGIN YLIOPISTO – HELSINGFORS UNIVERSITET - UNIVERSITY OF HELSINKI

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Tiivistelmä/Referat – Abstract

Ferromanganese concretions are commonly found in the Gulf of Finland forming in different sizes and shapes. The concretions are formed in various environments, where known factors contributing to their formation are e.g. the redox properties of the local environment, quality of the seabed associated with the concretions and bottom currents. Ferromanganese concretions are formed by natural geochemical processes, catalyzed by micro-organisms, e.g. archaea and bacteria.

The materials of this study were based on altogether 200 samples consisting of sample descriptions, underwater photographs and videos from the northern Gulf of Finland provided by GTK. Environmental variables used in this study were water depth, sediments associated with the concretions, seabed structure type, slope, roughness, distance to coast and distance to river, surface wave exposure, bottom wave exposure and bottom current velocity (m/s). The concretions were categorized into different groups, their distribution was illustrated on a map and environmental variables were used to determine which factors contribute to their formation and to elucidate the characteristics of the environments where each concretion type is formed.

Discoidal concretions were the most common concretion type in the study area indicating that the environment of the northern Gulf of Finland is most suitable for these concretions. Discoidal concretions were most commonly found on crests which was also the dominant seabed structure type in the study area. The results show that each concretion type is formed in an environment where certain environmental factors are commonly present. Spheroidal concretions (2–7 mm) were practically missing in the study area which is likely linked to the quality of the seabed and availability of Mn. Buckshot concretions were commonly found in the proximity of the coast, in calm, sheltered and heterogenic environments. Discoidal concretions were found to form in high energy and dynamic environments. The occurrence of crust concretions is likely linked to (high) water depth, relatively high bottom currents and clayey sediments. Irregular and spheroidal concretions (20–600 mm) represent most likely transient or irregular forms of spheroidal concretions forming in unstable conditions.

The economic interest towards ferromanganese concretions is likely to grow in the future. The high geodiversity of the seabed in the northern Gulf of Finland is possibly linked to the abundance and diversity of ferromanganese concretions however their ecological significance to the ecosystem is not yet fully understood.

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Ferromanganese concretions, Gulf of Finland, discoidal, seabed substrate, wave exposure, seabed structure, wave exposure

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Tiivistelmä/Referat – Abstract

Suomenlahden alueella esiintyy runsaasti rautamangaanikonkreetioita, jotka voidaan jakaa koon ja muodon perusteella eri tyyppeihin. Konkreetiota esiintyy vaihtelevissa ympäristöissä, joissa eri konkreetiotyyppien muodostumiseen tiedetään vaikuttavan useat eri tekijät, kuten alueen redox-potentiaali, merenpohjan laatu sekä pohjan virtaukset. Konkreetiot muodostuvat luonnollisten geokemiallisten prosessien seurauksena mikro-organismien, kuten arkeonien ja bakteerien katalysoimina.

Tämän tutkimuksen materiaalit perustuvat GTK:n keräämään aineistoon pohjoiselta Suomenlahdelta. Aineisto koostui näytekuvauksista, valokuvista sekä videoista, joita oli yhteensä 200 näytepisteeltä. Tutkimuksessa käytettyjä ympäristömuuttujia olivat veden syvyys, sedimentit, pohjan muototyyppi, korkeusgradientti (slope), pohjan topografinen vaihtelevuus (roughness), etäisyys lähimpään jokeen ja rannikkoon, pinnan aaltoekspositio, pohjan aaltoekspositio sekä pohjan virtausnopeus (m/s). Konkreetiot luokiteltiin eri kategorioihin ja niiden esiintymistä tutkimusalueella havainnollistettiin kartalla. Konkreetioiden muodostumiseen vaikuttavia tekijöitä sekä niille tyypillisen ympäristön olosuhteita arvioitiin ympäristömuuttujien avulla.

Kiekkomaisia konkreetioita esiintyi muita konkreetiotyyppejä enemmän, joka viittaa siihen että tutkimusalueen ympäristö soveltuu parhaiten tämän konkreetiotyypin muodostumiseen. Kiekkomaisia konkreetioita esiintyi eniten kohoumilla, joka oli vallitseva pohjanmuoto tutkimusalueella. Tulokset viittaavat siihen, että jokainen konkreetiotyyppi muodostuu ympäristössä, jossa vallitsee tietyt olosuhteet. Pallomaisia (2–7 mm) konkreetioita ei esiinny tutkimusalueella juuri lainkaan, joka liittyy luultavasti alueen pohjan laatuun sekä mangaanin saatavuuteen. Haulimalmi konkreetioita esiintyi rannikon läheisyydessä, rauhallisissa, suojaisissa ja heterogeenisissa ympäristöissä. Kiekkomaiset konkreetiot muodostuvat korkea-energisissä ja dynaamisissa ympäristöissä. Levymalmin muodostumiseen vaikuttavia tekijöitä ovat mm. veden syvyys, suhteellisen suuri veden virtausnopeus pohjalla sekä pohjan sedimentit (savi). Epäsäännöllisen muotoiset konkreetiot ja pallomaiset konkreetiot (20–600 mm) ovat todennäköisesti ns. väliaikaisia tai epäsäännöllisiä pallomaisia konkreetioita, joita muodostuu epävakaissa olosuhteissa.

On todennäköistä, että kiinnostus rautamangaanikonkreetioiden taloudelliseen hyödyntämiseen kasvaa tulevaisuudessa. Suomenlahden pohjan luonnon monimuotoisuus on mahdollisesti sidoksissa konkreetioiden laatuun ja esiintymisen laajuuteen, mutta niiden merkitys ekosysteemille ei ole vielä täysin selvää.

Avainsanat – Nyckelord – Keywords
Rautamangaani konkreetiot, rautamangaanisaostumat, Suomenlahti, kiekkomainen konkreetio, merenpohjan maalaji, merenpohjan rakenne, aaltoekspositio, bathymetric position index (BPI)

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CONTENTS

1. INTRODUCTION

Ferromanganese concretions are commonly found in the world's second largest brackish-water basin Baltic Sea (BS) and especially in the Gulf of Finland (GOF), Gulf of Bothnia (GB) and Gulf of Riga (Winterhalter 1966, Ingri 1985, Glasby et al. 1997). They are found in the world oceans too e.g., the Pacific Ocean (Hu et al. 2000). Ferromanganese concretions are known to accumulate various elements such as Fe, Mn and P (Ingri 1985, Baturin 2008) and anthropogenically derived environmental pollutants e.g. Pb, Zn and Cu (Zhamoida et al. 2007). Concretions are produced by natural geochemical processes, catalyzed by micro-organisms, e.g. archaea and bacteria (Zhang et al. 2002, Yli-Hemminki et al. 2014). Other factors contributing to the formation of ferromanganese concretions are e.g. redox properties of the local environment, bottom currents and the sediments associated with the concretions (Glasby et al. 1997). Ferromanganese concretions form hard physical structures at seabed, most likely compliant at with the EU's Habitats Directive habitat type 'Biogenic reefs', providing ecosystem services for numerous organisms. However their ecological significance is still relatively poorly known. Ferromanganese concretion bottoms were listed in the second assessment of threatened habitat types in Finland that was conducted between 2016 and 2018 (Kontula and Raunio 2018). Ferromanganese concretion bottoms were classified as Data Deficient (Kotilainen et al. 2018a, 2018b), which shows that knowledge of this marine habitat type is still incomplete. The economic potential of these concretions has been of interest for a long time. The first experimental ferromanganese concretion extraction in the Baltic Sea took place in 2006–2008 in the eastern GOF which did not contrary to preconceptions lead to concretion restoration. Concretions remaining in the extraction site had different geochemical structures compared to samples from undisturbed areas most likely due to the extraction and subsequent change in sedimentation conditions, mud accumulation and concretion burial. Ultimately this lead to the concretions becoming a secondary source of pollution in the extraction site (Zhamoida et al. 2017).

Early studies in the GOF, GB and in the North Baltic were conducted by Gripenberg (1934) who studied the sediments of the BS and described specimens of iron concretions found adjacent to the sediments. The main focus was on the sediments however Gripenberg contemplated that the source of Fe and Mn in the concretions was the sediment on the bottom of the sea rather than the surrounding water. Later Manheim (1965) published the first study describing the ferromanganese concretions in the BS. Winterhalter (1966) studied and described in detail the morphology, chemistry, mineralogy and formation of ferromanganese concretions of the GB and the GOF. Several studies of the composition (Ingri 1985, Anufriev et al. 2005, Anufriev and Boltenkov 2007), formation (Ingri and Ponter 1986) and ages and growth rates (Suess and Djafari 1977, Anufriev et al. 2005, Anufriev and Boltenkov 2007, Grigoriev et al. 2013,) of Baltic Sea ferromanganese concretions have been conducted since the early studies.

The ferromanganese concretions can be divided into different categories according to their morphology: buckshot concretions (< 2mm), spheroidal concretions (2–30 mm), irregular or transient forms of ellipsoidal or spheroidal concretions (15–60 mm), discoidal concretions (up to 40–70 mm in diameter), large flat crust concretions (up to 200–300 mm in diameter and 10–50 mm thick) and irregular crust concretions (Zhamoida et al. 2004). Abundant concretion fields are located at the border area between areas of anoxic silty-clayey muds and poorly sorted clayey sands forming in stable oxidizing conditions. Spheroidal concretions are especially common in these areas (Zhamoida 2007). Ferromanganese concretions are generally found at depths of ~20–100 m however in some areas of the eastern GOF the concretions can be found as shallow as three meters (Zhamoida et al. 2004).

The main constituents of ferromanganese concretions are Fe and Mn (Mn-oxides, Fe-oxides, Fe-hydroxides and Fe-oxyhydroxides) that form distinct banding in the concretions. The Fe is usually as goethite or amorphous phase and common manganese phases are birnessite and manganosite of which the formation of the latter may be bacterially mediated (Zhang 2002). Typically the geochemical structure of ferromanganese concretions in the GOF can be subdivided into four elemental associations. The associations are Mn-Mo-Ba and W-Zn-Cu-Ni which are closely related, Fe-P and a terrigenous group Si-Na-Al-Ti (Zhamoida et al. 2017). The contents of Fe and Mn are similar to oceanic nodules however there are some differences in the trace elements as the concentrations of e.g. Ti, Cu and Ni are significantly lower in ferromanganese concretions compared to average oceanic concentrations (Anufriev and Boltenkov 2007). The chemical composition of ferromanganese concretions depends on several factors: geography of the basin, salinity, depth, rate of sedimentation, growth of concretions and redox properties (Anufriev et al. 2005). Usually there are noticeable differences in the chemical composition of different concretion morphologies; spheroidal concretions have the highest Mn values whereas crust and discoidal concretions exhibit the highest Fe and lowest Mn concentrations (Zhamoida et al. 1996, Winterhalter 2004). The Mn/Fe ratio is dependent of factors such as the location and water depth of the concretion field (Zhamoida et al. 1996, 2017) and the ratio also varies in relation to the size of spheroidal concretions: bigger nodules have smaller Mn/Fe ratios. Hence the Mn/Fe ratio is an indicator of the environmental conditions as well as an indicator of the concretion type (Winterhalter 2004). Concretions can also shift their position on the seafloor due to slumping or bottom currents to the foot of slopes leading to changes in the chemical composition (Dean et al. 1981).

The aim of this study:

1. Gather the information on ferromanganese concretions supplied by GTK; classify the ferromanganese concretions into different categories and to illustrate their distribution in the GOF.

2. Study the influence of the environmental factors (depth, sediments associated with the concretions, seabed structure type, slope and roughness, distance to coast and distance to river, surface wave exposure, bottom wave exposure and bottom current velocity) on the formation of ferromanganese concretions and the formation of different concretion types and to elucidate the characteristics of the environments where each concretion type is formed.

2. GEOLOGICAL AND HYDROGRAPHICAL SETTING OF THE GULF OF FINLAND

2.1 The development of the modern Baltic Sea

The Baltic Sea is located in a depression in the Precambrian crystalline basement rock. The characters of the modern Baltic Sea seafloor were developed by the influence of pre-glacial bedrock surface and processes related to it, glacial erosion and deposition and postglacial sedimentary processes (Winterhalter et. al. 1981, Kaskela and Kotilainen 2017). The development of the Baltic Sea started ca. 17–16 ka BP when the embryo of deglacial Baltic Ice Lake formed (Houmark-Nielsen and Kjaer 2003, Stroeven et al. 2016). The following warming at the start of the Holocene Epoch is more or less connected to the onset of the Yoldia Sea stage ca. 11 700 ka BP (Walker et al. 2009, Andrén et al. 2011). The Yoldia Sea stage can be characterized by rapid ice sheet retreat which was followed by brackish and freshwater phases. The isostatic rebound in the area of southern Sweden caused the waters of the Yoldia Sea to be trapped marking the end of this stage and the beginning of the Ancylus Lake stage (Andrén et al. 2011). The Anculys Lake stage ca. 10 700 - 9 800 ka BP was followed by the Littorina Sea stage when first signs of marine influence were present since the Yoldia Sea (Andrén et al. 2011). According to Andrén et al (2000) the beginning of this stage is called the Initial Littorina Sea because the Baltic Sea was at level with the world ocean and the salinity was low. During this stage the Scandinavian ice sheet melted completely (Andrén et al. 2011) and eventually the Baltic Sea reached its present salinity levels ca. 2000 - 1000 BP (Andrén et al. 2000, Warnock et al. 2017, Stepanova et al. 2019).

2.2 The geography and hydrography of the Gulf of Finland

The GOF is very shallow sub basin of the BS with an average depth of 37 m. This brackish water basin is connected to the Baltic Proper without any physical barrier

(Leppäranta and Myrberg 2009). The bedrock of the GOF is divided into two domains; northern part consisting of Precambrian crystalline rocks whereas the southern area is dominated by Phanerozoic sedimentary rocks (Glasby et al. 1997, Koistinen et al. 2001). The morphology is mainly preglacial in origin however glacial erosion and deposition have had noticeable impact on the topography. Glacio-isostatic rebound and modern sedimentation are ongoing processes affecting the topography (Glasby et. al 1997, Kotilainen et al. 2016). In the eastern tail of the GOF at the mouth of the Neva Bay the mean water depths is <5 m gradually increasing towards the west (Leppäranta and Myrberg 2009).

The main feature of the seafloor of GOF is the fragmental nature of the different bottom and substrate types (Kankaanpää et al. 1997, Kaskela et al. 2012, Kaskela and Kotilainen 2017). The bottom features include such as basins, plains, elevations and valleys. The sediments in the different geomorphological features vary form fine sediments to coarser sediments (Kaskela et al. 2012) and are represented mainly by glacial sediments such as fluvial material and varved clays and silts or post-glacial sediments that were deposited during limnic and brackish-water phases of the BS (Kaskela et al. 2017).

The hydrography of the GOF is highly complex and the oxygen conditions vary seasonally. The GOF receives saline water from the seaward end in the west and fresh water from rivers in the east of which the River Neva is most significant (Alenius et al. 1998). This water exchange creates a strong and permanent salinity gradient (Perttilä et al. 1995, Leppäranta and Myrberg 2009, Vallius et al. 2011). The salinity increases from the east to the west ranging from 0‰ to 9‰ (Alenius et al. 1998). The river Neva discharge is approximately 75% (18% of the whole Baltic Sea, Leppäranta and Myrberg 2009) of the total freshwater input to the GOF (Pitkänen et al. 2008) and it includes the most severe loading of the whole BS (Alenius et al. 1998). However the Vyborg Bay area and Kymijoki are also significant carriers of heavy metals especially in the eastern part of the GOF (Vallius et al. 2007).

In the BS area the seasonal thermocline in the summer and especially the salinity define the stratification of the water masses (Alenius et al. 2016). The halocline is strongest in the western parts of the GOF and it is found at depths of 60–80 m (Leppäranta and Myrberg 2009, Alenius et al.1998). In the eastern parts of the GOF the halocline eventually disappears due to the strong mixing caused by the River Neva discharge (Perttilä et al. 1995, Pitkänen et al. 2003). The bottom layers are often stranded by the halocline (Leppäranta and Myrberg 2009) and mixing of the bottom water masses is confined to the autumn and early winter mixing (Alenius et al. 2016).

Sediments have a good capacity to release and retain nutrients (Pitkänen et al. 2008) and in the GOF the surface sediment organic matter and nitrogen concentrations are relatively high in the Baltic Sea area (Lehtoranta 2003). The ferromanganese concretions are also good traps for various elements such as phosphorous which is closely related to Fe (Ingri 1985) and it is estimated that concretions in the eastern GOF contain significant amounts of P (Vallius et al. 2011). During hypoxia Fe-oxide bound P of surface sediments is shown to act as an internal source for P (Mort et al. 2010, Jilbert et al. 2011). The concretions also have 1.5–5 times higher concentrations of most metals compared to the average seafloor surface gyttja clays (Vallius et al. 2011) and the concentrations of e.g., Pb, Zn and Cu in the surface micro-layers of concretions have increased 3–5 times due to anthropogenic influence (Zhamoida et al. 2007). The seafloor of the GOF is prone to anoxia and the high organic matter content of the surface sediments increase the anoxia by breakdown of these sediments (Pitkänen et al. 2008, Vallius et al. 2011). In the GOF the anoxia is considered a natural phenomenon occurring seasonally and also as a permanent state of the waters below the halocline. Ferromanganese concretions are sensitive to changes in environmental conditions and the permanent anoxia could spread to the areas of ferromanganese growth leading to the dissolution of the concretions and the release of phosphorous and other harmful substances to the sea which further deteriorates the already poor state of the GOF. (Vallius 2011)

Abundant concretion fields can however partially control the redox conditions of the environment. The concretions fields are located at the margins of anoxic and stable oxic conditions in the sediments. The concretions can restrain the oxygen content fluctuations in near bottom waters and sediments by the transformation of Mn^{2+} to Mn^{4+} and back. If the concretion growth seizes, it can lead to the dissolution of the concretions and subsequent re-pollution of the bottom waters (Zhamoida et al. 2007). Yli-Hemminki et al. (2014) also point out that the concretions and the bacteria they host may have noticeable impact on the biochemical cycles of Fe, Mn, P and other harmful metals in the BS. This is because of their abundance, physical and geochemical properties and the fact that the bacteria colonized by the concretions are able to participate in the oxidation of Mn and Fe.

3. THE FERROMANGANESE CONCRETIONS IN THE GULF OF FINLAND

3.1 The source of Fe and Mn and the formation of ferromanganese concretions

The Fe and Mn are transported to the Baltic Sea by weathering of silicate rocks and by fluvial processes, eventually accumulating to the seafloor (Winterhalter 2004, Raiswell and Canfield 2012) as colloidal or suspended particles (Krachler et al. 2005). The Neva river is likely to be one source of these elements especially in the eastern GOF where the Mn-rich spheroidal concretions are abundant. The Neva river discharge is spread around the GOF in an anti-clockwise direction and as the colloidal particles mixed with freshwater reach the sea, the seawater neutralizes the surface charges of the particles resulting in precipitation (Zhamoida et al. 1996). Another possible source of Fe and Mn is the glacial till covering the basin of the GOF; Fe and Mn are substantial constituents of glacial till and are there for considered to be a source for these elements (Ingri 1985). In the Baltic proper the Mn and Fe are enriched in basinal waters below the halocline due to anoxic conditions. The inflows from the North Sea bring oxygenated water and transport Mn and Fe and other metals from the bottom waters to oxygenated areas where they can be incorporated in concretion formation (Emelyanov 1986). This is thought to be the main source of Fe and Mn for spheroidal concretions in the Baltic Proper where the inflows from the North Sea reach the bottom waters (Zhamoida et al. 2007).

There are evidence that the formation of ferromanganese concretions is however not entirely the effect of physico-chemical precipitation (Zhang 2002). Studies from the GOF (Zhang 2002, Yli-Hemminki et al. 2014) and from the Pacific Ocean (Hu et al. 2000) show that the formation of spheroidal ferromanganese concretions is connected to bacterial activity. Several different bacteria were found both inside and on the surface of spheroidal concretions from the GOF. The bacteria in the concretions were able to participate in the oxidation of Mn and affect the formation of Fe oxides however only minority of these bacteria participates in the oxidation process (Yli-Hemminki et al. 2014). Nanobacteria scale filamental microstructures found in spheroidal concretions also suggest that the formation of the concretions is connected to biochemical processes (Zhang 2002).

Nevertheless the formation of ferromanganese concretions is a result of changes in the redox properties of the environment: Fe and Mn dissolve in reducing conditions, migrate upwards into the bottom waters, and precipitate under oxidizing conditions as oxyhydroxides (Ingri and Ponter 1986). The redox characteristics therefore control the distribution of Mn and Fe in the Baltic Sea area and are also connected to the morphology of the concretions (Glasby et al. 1997). In the Bothnian Sea for example where the redox levels are somewhat lower than in the Bothnian Bay, Fe-rich crust concretions are common while in the Bothnian Bay Mn-rich spheroidal nodules are abundant (Ingri and Ponter 1985). Increasing water depth increases the mobilization of manganese in the anoxic environment and therefor the highest Mn concentrations are found within the deepest concretion fields (Zhamoida et al. 1996). The processes affecting manganese adsorption include such as pH, reduction potential, the presence of Fe and Al oxides, salinity and temperature (Tebo et al. 2004). Spheroidal concretions are especially abundant in the eastern GOF where the mobilization and migration of manganese is more active. There the abundance of spheroidal concretions can locally reach 50–60 kg/m^2 (wet weigh) (Zhamoida et al. 2017). In addition to depth other factors controlling the formation of spheroidal concretions are the distance to the source of the compositional materials and the location of the concretions in the sediment column. The concretions are usually found in the upper part of the sediment column whereas dissolution takes place in the lower part of the sediment column (Zhamoida et al. 1996). Concretion formation is possible only in oxidizing conditions however anoxia in the GOF is common below the halocline (Vallius et al. 2011). This in addition to concretions being buried in the sediments can lead to the dissolving of the concretions. In these circumstances the concretions either dissolve completely or form unfamiliar forms of concretions (Zhamoida et al. 2007).

The growth rates of the concretions are geologically speaking fast (Zhamoida et al. 2007) and the bacteria that participate in the oxidation of Fe and Mn found in the ferromanganese concretions can partly explain these high growth rates (Yli-Hemminki 2014). There are several studies and methods concerning the growth rates and ages of ferromanganese concretions in the BS area. Studies from the GOF estimate the growth rates of spheroidal concretions to be 7.5–9 mm/ka (Anufriev et al. 2005 and Anufriev and Boltenkov 2007) by using helium isotopes and 14–60 mm/ka by using ^{210}Pb (Grigoriev et al. 2013 and Zhamoida et al. 2007). The ages of spheroidal concretions were estimated using ^{210}Pb isotope to be ca. 679–859 years (Grigoriev et al. 2013).

3.2 The morphology and associated environments of ferromanganese concretions in the Gulf of Finland

The sedimentological, geographical and hydrological conditions vary significantly in different parts of the Baltic Sea area. The morphology and distribution of different concretion types is connected to the underlying sediments and the relief of the seafloor (Zhamoida et al. 1996). Different morphological types of ferromanganese concretions are formed in specific environments of which two typical environments for concretions have been identified from the eastern GOF (Zhamoida et al. 1996, 2004).

3.2.1 Spheroidal and buckshot concretions

Mn-rich spheroidal and buckshot concretions are commonly found in concretion fields that are located at the margins of basins at depths of 20–100 m with a slope angle of 1–2 degrees. They are the most common concretion types in these fields though other concretion types can be found. The basins are covered by Late Holocene muds but in some cases the concretions can also be found at the margins of recent marine mud zones (Zhamoida et al. 1996). Usually the concretions are located at the sediment/water interface either covered by a thin layer of sediment or partially covered by the underlying sediment (Zhamoida et al.1996, Winterhalter 2004).

Spheroidal concretions (2–30 mm in diameter) are round or more often sub-rounded concretions consisting of concentric Mn-rich and Fe-rich layers and are usually found in the topmost sediment 50–150 mm deep. Usually there is a silty-clay mud covering the upper layer however in some cases the concretions are exposed at the seafloor (Zhamoida 2004). Especially in the area of spheroidal concretions sedimentation rates are usually low (Ingri 1985) and the bottom currents high (Glasby et al. 1997). Sometimes spheroidal concretions can form ellipsoidal or more round shaped concretions with dissolution features. These concretions can be bigger in size (15–60 mm) and are considered to be irregular or transient forms (Zhamoida 2004). In some cases the spheroidal concretions are known to have grown together to form a crust like formation (Winterhalter 2004).

Buckshot concretions (< 2mm) are small roundish shaped concretions. In the early studies (eg. Gripenberg 1934 and Winterhalter 1966) the buckshot and spheroidal concretions were usually classified as one and the same concretion type. Later the classification was extended to fit the modern classification limits.

3.2.2 Discoidal and crust concretions

Discoidal and crust concretions are commonly formed in areas that are located on the slopes of islands and shoals in areas of low sedimentation rate. In the eastern GOF these concretions are found at water depths of 3–60 m (Zhamoida et al. 2004). In the Bothnian Bay and Bothnian Sea the crust concretions have been found commonly quite deep (up to 92 m and 135 m, respectively). Discoidal concretions have been found up to 65 m deep in the Bothnian Sea (Winterhalter 1966). These concretions are not commonly abundant in the eastern GOF however occasionally concretions can be found accumulated at the foot of slopes as a result of lateral movement of the concretions (Dean et al. 1981). In the GOF area the crust concretions are found forming wide and solid layers which can be broken down to smaller pieces (Winterhalter 1966).

Discoidal concretions (40–70 mm in diameter, 4–10 mm thick) typically grow around a nucleus, a mineral grain for instance, forming a lateral growth pattern (Zhamoida 2004). These concretions are usually convex on the upper size and show dissolution features on the concave underside which indicates that the source of Mn and Fe originates from the underlying sediments rather than the surrounding seawater (Winterhalter 1966). Discoidal concretions are generally found on sandy sediments overlaying clayey or silty sediments (Winterhalter 2004).

Crust concretions are large flat crusts with granular surface texture (up to 200–300 mm in diameter, 2–50 mm thick) (Winterhalter 1966, Zhamoida 2004). Crusts can be further divided into two types; crusts that are fixed to e.g. rocks or remnants or glacial clay and a more or less coherent concretion formation varying from few millimeters to two centimeters in thickness (Winterhalter 2004). Crusts usually form darker and lighter layers up to few millimeters thick. Winterhalter (1996) suggest that the color changes are formed due to mineral grains and other compositional elements embedded in the crusts rather than due to changes in alternating Mn and Fe layers as seen in other concretion types. The underlying sediments are usually silty or clayey sediments (Winterhalter 2004). It is possible that the crusts form when there are no mineral grains for the discoidal concretions to form around or when the conditions for the formation of nodular concretions are absent. The formation of crusts is nevertheless the result of deposition of Mn and Fe oxyhydroxides directly from the surrounding sea water. Sometimes broken pieces of crusts can start to grow laterally in similar manner as discoidal concretions (Winterhalter 1966, 2004).

1 A. Buckshot concretions. Concretions on top of oxidized silt layer. Underneath, glacial clay with sand lenses. Seafloor structure basin. Photo: GTK

1 B. Spheroidal concretions, 0.5- 4 cm in diameter. Concretions were covered by a thin sediment layer, in muddy sand. Seafloor structure crest. Photo:GTK

1 C. Discoidal concretions covered 90% of the seafloor in the sampling area. 4-5 cm in diameter. Oxidised muddy sand in between nodules, underneath clay, stones and sand. Seafloor structure crest. Photo:GTK

1 D. Crust concretions that covered the whole seafloor in the sampling area. Up to 7 cm in diameter. Concretions were covered by muddy sand, underneath sandy clay. Seafloor structure crest. Photo:GTK

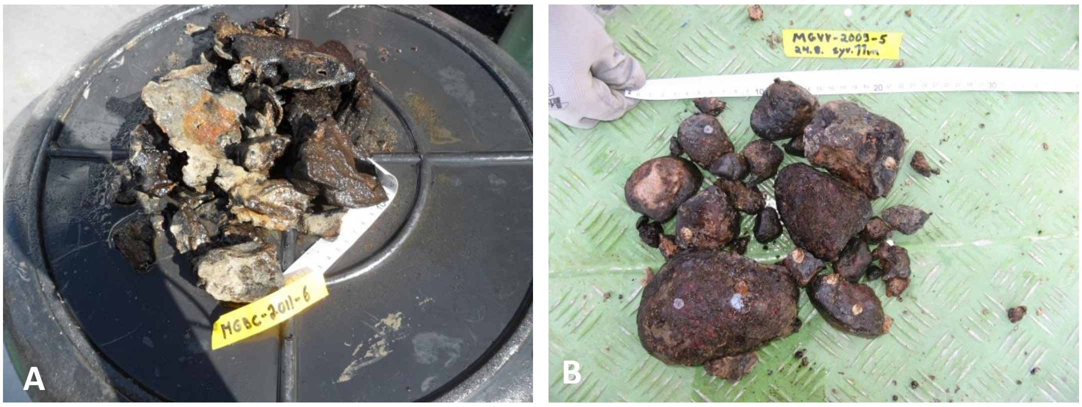

Figure 2. A. Pieces of crust concretions. The concretions formed a 1 cm thick layer on the surface of the seafloor. Erosional sand layer under the concretions, glacial clay below the sand. B. One sample of ferromanganese precipitate on a rapakivi granite. The bottom of the seafloor was covered by rocks 3 – 15 cm in diameter. The ferromanganese precipitates in the seafloor are seen in figure 3C. Photos: GTK.

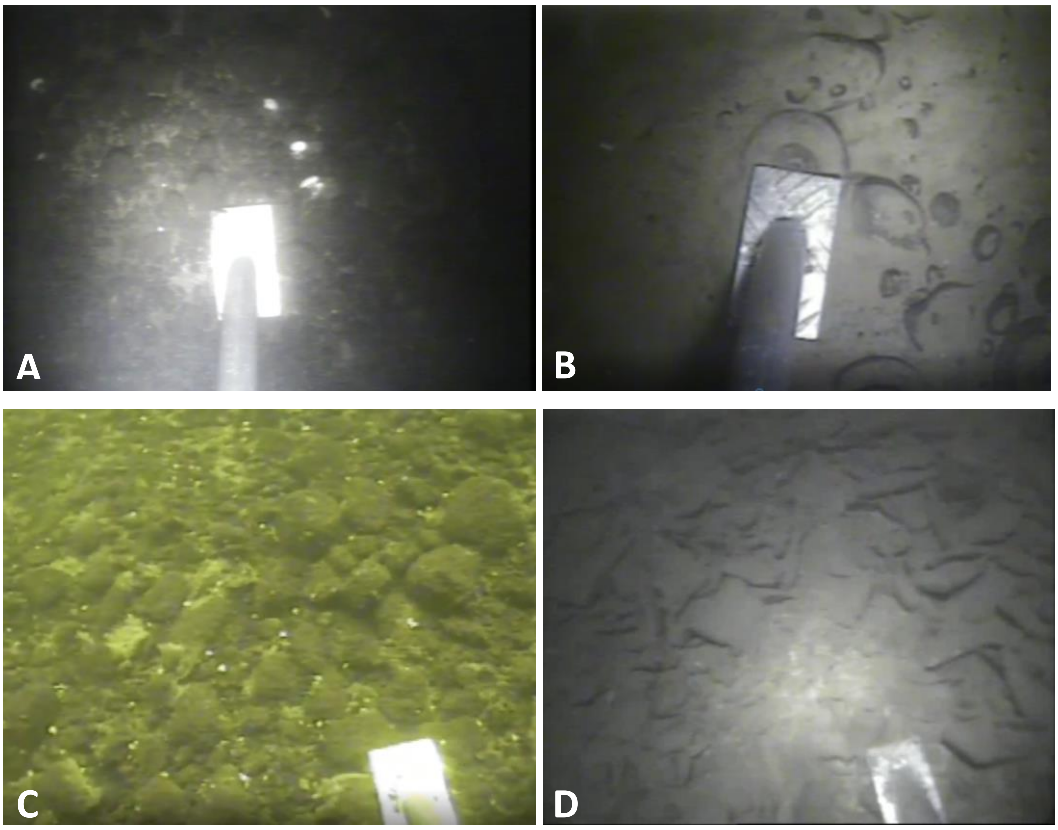

Figure 3. Concretions on the seafloor. A. Spheroidal and discoidal concretions, B discoidal concretions, C. ferromanganese precipitate covering rapakivi rocks, D crust concretions that are also seen in figure 1 D. Photos/videos: GTK.

4. MATERIALS AND METHODS

The materials of this study were supplied by Marine Geology Unit, the Geological Survey of Finland. The expeditions in the GOF were made during 1984–2003 and 2008–2012. The materials in this study are based on sample descriptions, photographs and videos which were made during the expeditions. The samples were collected with a box corer and with a Van Veen grab sampler. Both samplers are intended to underwater surface sediment sampling of which the box corer gives more undisturbed and therefore more reliable samples. The sampling sites in the GOF can be seen in figures 4, 5 and 6. The coordinates are in the WSG 84 UTM 35 N coordinate system.

4.1 Classification of the concretions

The ferromanganese concretions were categorized by using the classification by Zhamoida (2004). The concretion types and their descriptions are presented in Table 1. Some alterations in the classification were made because the samples were not available for closer observation. The sizes of some concretion types were changed because the samples did not fit the existing classification limits. An additional class was added for those concretions that had no specific description (concretions) and in this study irregular concretion type is not considered as a concretion type, rather a group of samples with irregular morphology (description below). Concretion samples deeper than 2 cm in the sediment column are not included. In addition some of the samples did not include information about the water depth in the sampling site or the bottom sediment/sediments. In some cases there was more than one concretion type in the same sampling site. These combination samples (16 samples) are treated separately because here the focus is on individual concretion types.

Table 1. Descriptions of different concretion types.

Concretion type	Description
Buckshot	< 2 mm in diameter, round or roundish shape.
Spheroidal 2 - 7 mm	2 mm–7 mm in diameter, round or roundish shape.
Spheroidal 20 – 600 mm	20 mm up to 600 mm in diameter. Round or roundish nodules. Majority of the concretions were 1–2 cm in diameter. Possibly irregular and/or transient forms.
Spheroidal (size unknown)	These concretions had no information about the size.
Discoidal	20 mm –80 mm in diameter. Flat, disclike concretions.
Crust	10 mm–700 mm in diameter. Flat shaped concretions.
Irregular	Concretions of irregular forms such as elongated concretions and helmet-like shaped concretions that did not fit any other category. These concretions were categorized into this group because they were not available for closer observations.
Concretion	No description of the size or shape of the concretions.

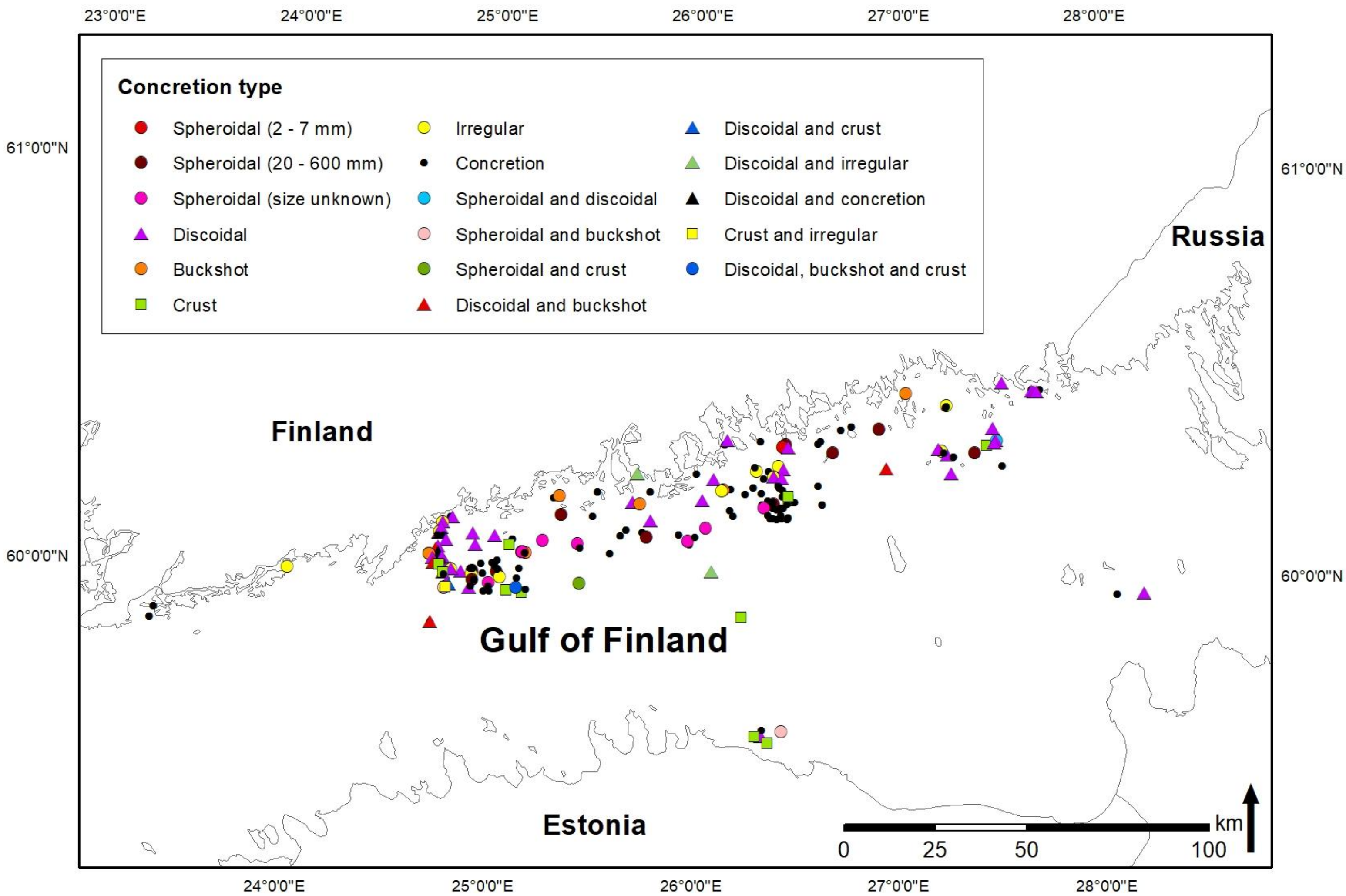

Figure 4. Map showing the sampling sites and the different concretion types. Map from HELCOM, OpenStreetMap.

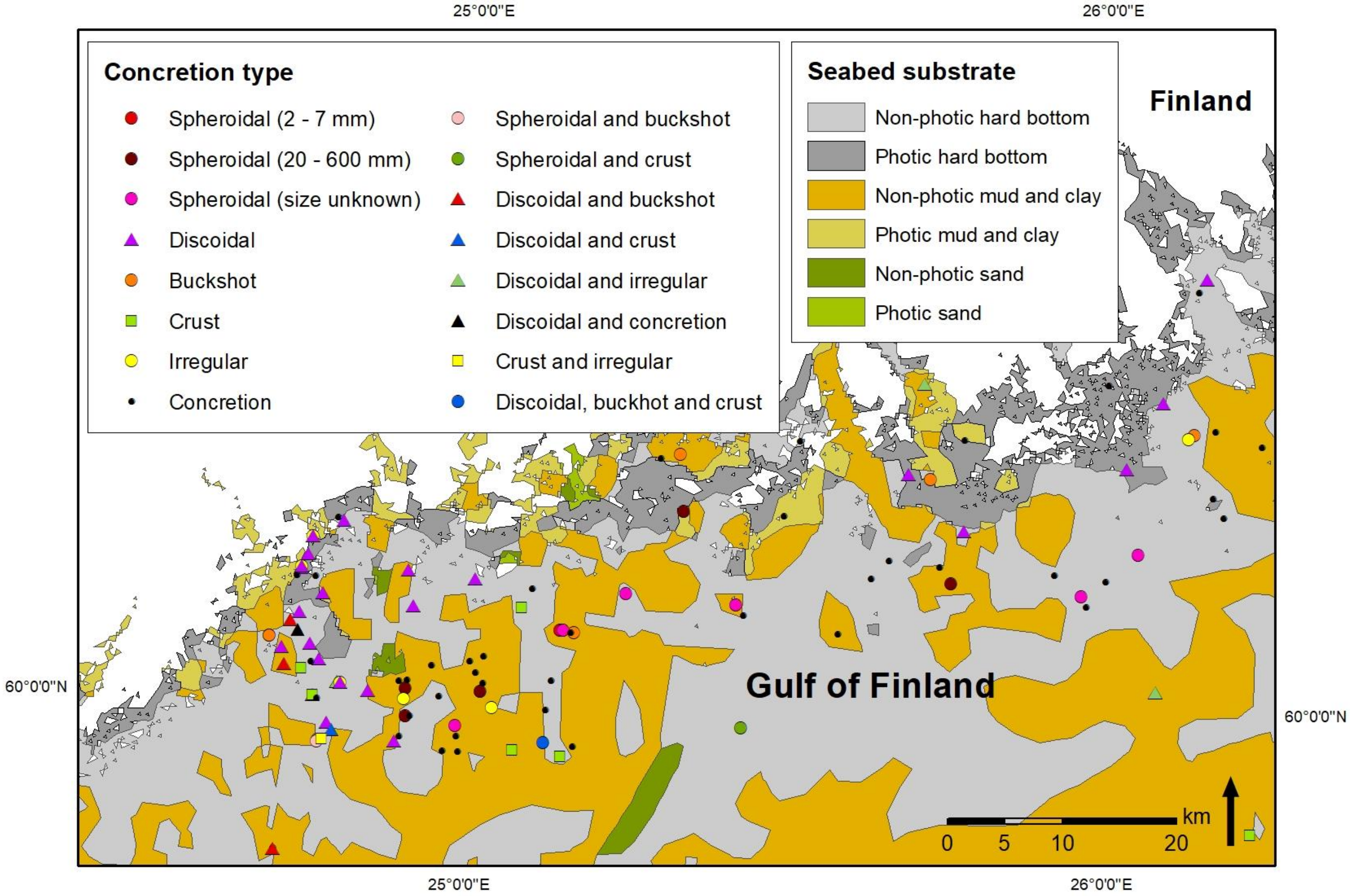

Figure 5**.** Samples on the western sampling area, concretion types and seabed substrate. Hard bottom includes: bedrock and hard bottom complex, patchy hard surfaces and coarse sand (sometimes also clay) to boulders, sand includes: fine to coarse sand (with gravel exposures) and mud and clay includes: hard clay sometimes/often/possibly exposed or covered with a thin layer of sand/gravel and gyttja-clay to gyttja-silt. Seabed substrate from HELCOM (DHI, EuSeaMap, BALANCE).

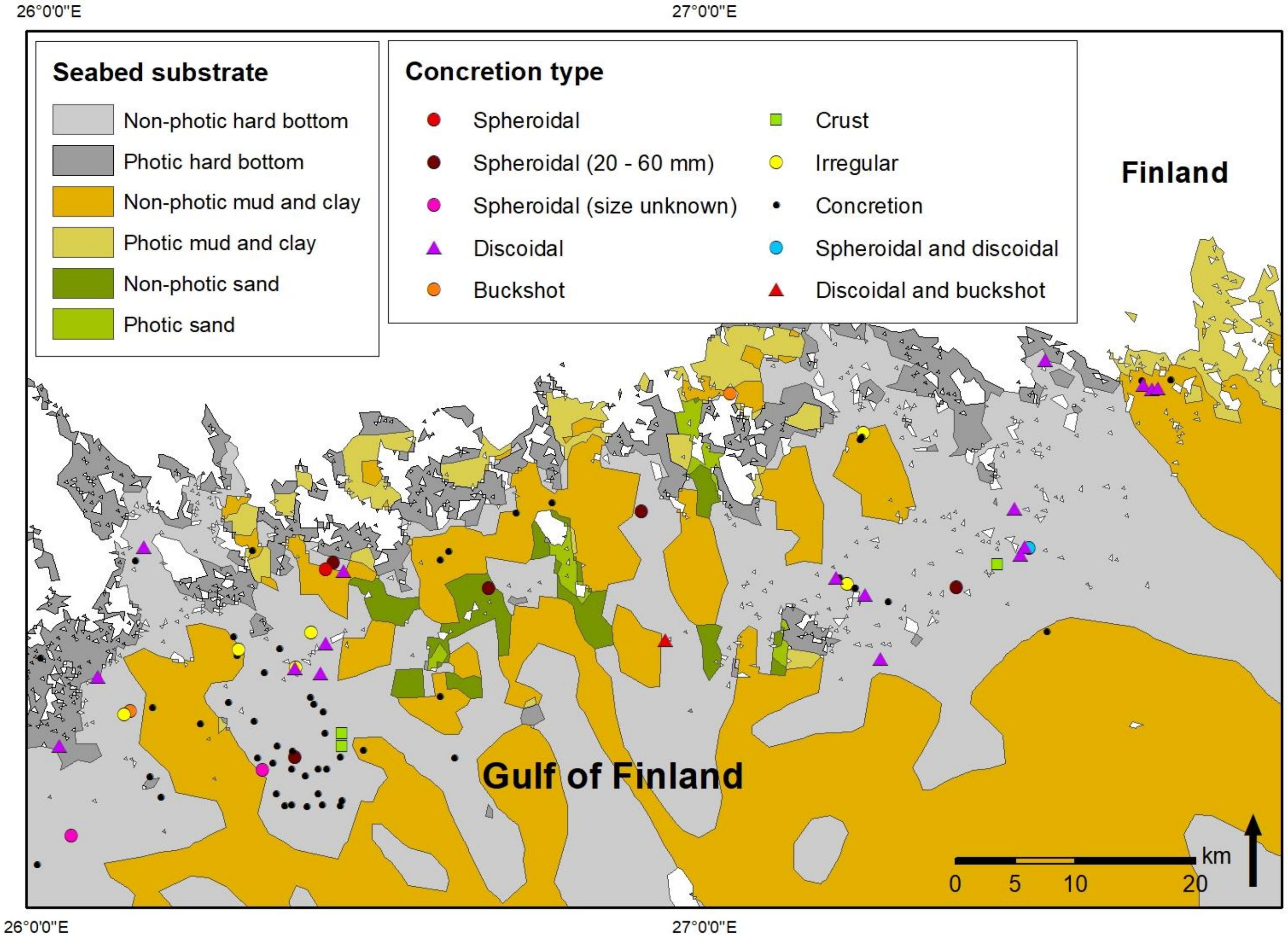

Figure 6**.** Samples on the eastern sampling area, concretion types and seabed substrate. Hard bottom includes: bedrock and hard bottom complex, patchy hard surfaces and coarse sand (sometimes also clay) to boulders, sand includes: fine to coarse sand (with gravel exposures) and mud and clay includes: hard clay sometimes/often/possibly exposed or covered with a thin layer of sand/gravel and gyttja-clay to gyttja-silt. Seabed substrate from HELCOM (DHI, EuSeaMap, BALANCE)

4.2 Environmental variables

The sample descriptions and environmental variables can be seen in Table 2 and Table 3. The environmental variables used in this study are water depth, sediments associated with the concretions, seabed structure type, slope, roughness, distance to coast, distance to river, surface wave exposure, bottom wave exposure and bottom current velocity. In addition to these variables one of the most important factor controlling the formation and preservation of ferromanganese concretions are the redox conditions of the local environment (Ingri 1985, Glasby 1997). Accurate seawater oxygen concentration data in the sampling area was not available at the time of this study.

Table 2. Environmental variables and their definitions. Slope, roughness, distance to coast, distance to river by Kaskela and Kotilainen 2017. Bottom current produced by the BALANCE project.

Variable	**Description**
Depth	Water depth of the sampling site
Sediment on top of the concretions	The sediment type found on top of the concretions
Sediment below the concretions	The sediment where the concretions were found embedded in or the sediment right below the concretions.
Sediment on the bottom	The bottom sediment which had no direct contact with the concretions
Seabed structure	Seabed structure of the sampling location (see Table 3 below)
Slope	Rate of change in bathymetric depth
Roughness	Standard deviation of slope calculated for areas having a radius of 20 km
Distance to coast	Euclidean distance to closest coast
Distance to river	Euclidean distance to closest river
Surface wave exposure	The influence of the waves on the sea surface
Bottom wave exposure	The influence of the waves on the bottom of the sea
Bottom current	Bottom current velocity m/s

4.2.1 Sediments

The sediments were classified according to the sample descriptions. The sediment on top of the concretions was either a thin layer of sediment above the concretions or the sediment where the concretions were embedded in. If the concretions were embedded in the sediments, the topmost sediment and the sediment below the concretions were the same. The bottom sediment is the sediment below the layer where the concretion was found and this layer had no direct contact with the concretions. The sediment data is point-source information as it originates from the sediment samples. The spatial resolution is high, and the sample locations are based on DGPS –positioning.

Table 3. Seabed structure types by Kaskela et al. (2012).

Seabed structure type (BPI) and distribution in the GOF (%)	**Description**	**Substrate**
Crest (32%)	Elevations of seafloor including plateaus, hills, banks and sills	Sand, clay and hard clay, moraine formations Bedrock and boulders
Basin (33%)	Depression in the seafloor, more or less equivalent dimensional in plain and of variable extent	Mud and clay Coarse substrates
Valley and trough (10%)	Troughs are steep sided, long depressions in the seafloor. Valleys are steep sided small depressions or relatively shallow depressions	Mud and clay Coarse substrates
Plain (25%)	Large areas where relief stays low and homogenous	Mud and clay Coarse substrates

4.2.2 Seabed structure type

The seabed structure types (BPI, bathymetric position index by Lundblad et al. 2006) are modified to fit the BS environment with a point density of 200 by 200 m (Kaskela et al. 2012). The seabed structure types each include substrates that are seen in table 3. Coarse substrates include hard clay, sand, complex sediments combined and bedrock. Plains and basins cover over half of the GOF seafloor, elevations cover nearly third and valleys and holes cover one tenth of the surface of the GOF. (Kaskela et al. 2012)

4.2.3 Slope and roughness

The slope and roughness describe the overall effect of geological processes such as bedrock faulting, pre-glacial erosion and glacial erosion and accumulation. Surface roughness is most effectively described with the slope with 20 km radius (Kaskela et al. 2017 and Grohmann et al. 2011).

4.2.4 Distance to coast and distance to river

Distance to coast and distance to river elucidate the influence of beach and near shore processes and the supply of fluvial material such as Fe from the continents (Kaskela and Kotilainen 2017).

4.2.5 Wave exposure

The wave exposure values were obtained from Kaskela and Kotilainen (2017). The values are based on wave exposure grids for the Finnish coast calculated by Isaeus and Rygg (2005). Wave exposure is among the most important mechanisms structuring the archipelago environment (Isaeus and Rygg 2005). The seabed sediments in the shelf area are eroded and transported mainly by tides, wind-generated waves, bottom currents and ice. Energy in the seafloor is derived from the wind-induced surface waves that eventually reach the bottom of the sea (Kaskela and Kotilainen 2017). The wave-energy effects sedimentation down to ~70–80 m deep in the Baltic Sea (Kohonen and Winterhalter 1999, Jönsson et al. 2005).

Surface wave exposure (SWE) values cover the surface of the sea which takes into account obstacles such as islands and skerries. It describes how sheltered the surface area is: the SWE increases with depth indicating that when moving towards the center of the GOF where there surface of the sea is more open the values increase as the depth tends to increase when going offshore. In sheltered archipelago areas the SWE values are smaller than in the open sea.

In the same manner bottom wave exposure (BWE) values are commonly smaller in deeper areas such as in the middle of the GOF where the bottom is sheltered and in contrast bigger values are obtained in open areas such as crests that are elevated features on the bottom of the sea. Uniform values indicate areas of low relief seabed structures.

4.2.6 Bottom current velocity

Currents in the sea are generated by different parameters such as tidal motion, wind stress, density differences due to differences in salinity or temperature, seismic activity and motion of the earth in near shore regions. Currents in the shore areas are usually wave-induced and when moving off the archipelago area the tidal and meteorological forces are the most important current generating parameters. Close to the sea bottom a turbulent layer forms due to the friction of the bottom current. This layer varies from few meters to several tens of meters in thickness. The current speed increases nonlinearly with the height above the seabed so that near the bottom the current speed is zero increasing to maximum values towards the top layer. (NERI, BALANCE, Bendsten et al. 2007.)

5. RESULTS

5.1 Sources of error

The classification of the concretions in this study was carried out by examining the sample descriptions, pictures and videos (if available). Pictures and videos were used to confirm the concretion type and sediments mentioned in the description. It is possible that some samples are classified incorrectly especially if there were no pictures to confirm the concretion type.

Bulk of all samples had no sediment covering the concretions. Especially spheroidal concretions (table 5) are often found covered by a thin layer of silty-clay mud (Zhamoida 2004) and the results show that only 10 % of the samples were covered by muddy sand. The absence of the sediments above the concretions is most likely due to the sampling method. The samples were collected with Van Veen grab sampler and a box corer which can cause the fine grained topmost sediment to wash away or leaving only the coarser grained sediments on top of the concretions. Figure 3 shows the concretions on the seafloor and especially in the Figures 3B, and 3D the thin layer covering the concretions is clearly visible.

The environmental variables such as slope and roughness might not represent the smaller scale environments to their full extent due to the broad-scale resolution of the variables (Kaskela and Kotilainen 2017).

5.2 The sedimentary environment

Number of samples, water depths and seabed structure types of different concretion types can be seen in Table 4. The water depth of all samples ranges from 9,9 m to 65 m. Crust concretions are found deeper than any other concretion type. Discoidal concretions are the most abundant concretion type (20,5 % of all samples) while some concretion types had a very low number of samples. Majority of the samples (108/200) are found on crests and especially discoidal concretions are abundant in these areas. Valleys and troughs are the most uncommonly associated seafloor structure type with ferromanganese concretions however spheroidal concretions are found most frequently in these areas when comparing to other concretion types-

5.2.1 Spheroidal and buckshot concretions

The bigger spheroidal concretions (20–600 mm) are likely to represent irregular and/or transient forms of spheroidal concretions as they were up to 6 cm in diameter. Majority of these samples were 1–3cm in diameter. Sampling sites of all spheroidal concretions were found to have various sized concretions in the same site of which majority were 1–2 cm in diameter and only two samples having a diameter of 4–6 cm. Detailed descriptions of surface texture and shape of the concretions were unknown and therefore they were not categorized as transient forms as in the Zhamoida et al. (2004) classification. Sediments associated with spheroidal concretions can be seen in Table 5. The topmost sediment was missing in majority of the samples. Bigger concretions (20–600 mm) were most commonly found on clay or clayey sediments and the smaller concretions (2–7 mm) on muddy clay or sand. The bottom sediments were clay in majority of the samples. The bigger spheroidal concretions (20–600 mm) were most abundant of all spheroidal concretions and also had the widest depth range as seen in Figure 7.

On average, buckshot concretions were found in relatively shallow water. The topmost sediment was either muddy sand or silt. These concretions were found on all bottom structure types and found mostly on clayey sediments underlain by clay.

Table 4. Water depths of different concretion types and the associated seafloor structure type. Seafloor structure types from Kaskela and Kotilainen 2017.

Concretion type	**Depth (m)**			**Seabed structure**					
	Mean	Minimum	Maximum	Crest	Basin	Valley and trough	Plain	Number of samples	
Buckshot	31,0	12,0	49,0	2	2	1	2	**7**	3,5 %
Spheroidal 2-7 mm	37,5	27,0	48,0	0	0	1	1	**2**	1 %
Spheroidal 20-600 mm	31,3	15,5	45,9	3	1	2	4	**10**	5%
Spheroidal (size unknown)	45,6	39,0	52,0	2	2	2	1	**7**	3,5%
Spheroidal (all samples)	37,2	15,5	52,0	5	3	5	6	**19**	**9,5%**
Discoidal	29,1	9,9	53,9	31	6	1	2	**41**	20,5 %
Crust	49,3	25,3	65,0	6	3	0	2	**11**	5,5 %
Irregular	29,1	9,9	55,0	7	3	2	0	**12**	6 %
Concretion (no description)	36,9	9,9	60,0	49	16	10	16	**94**	47%
Spheroidal and buckshot	53,0	51,0	54,9	3	0	0	0	**3**	1,5 %
Spheroidal and crust	45,0			0	0	1	0	**1**	0,5 %
Spheroidal and discoidal	39,9			1	0	0	0	**1**	0,5 %
Discoidal and buckshot	38,7	18,4	56,9	1	2	0	1	**4**	2 %
Discoidal and crust	42,4			0	1	0	0	**1**	0,5 %
Discoidal and concretion	27,9			1	0	0	0	**1**	0,5 %
Discoidal and irregular	35,9	13,9	59,0	0	1	0	2	**3**	1,5 %
Crust and irregular	44,5			1	0	0	0	**1**	0,5 %
Discoidal, buckshot and crust	63,4			1	0	0	0	**1**	0,5 %
Number of samples				**108**	**37**	**20**	**31**	**200**	

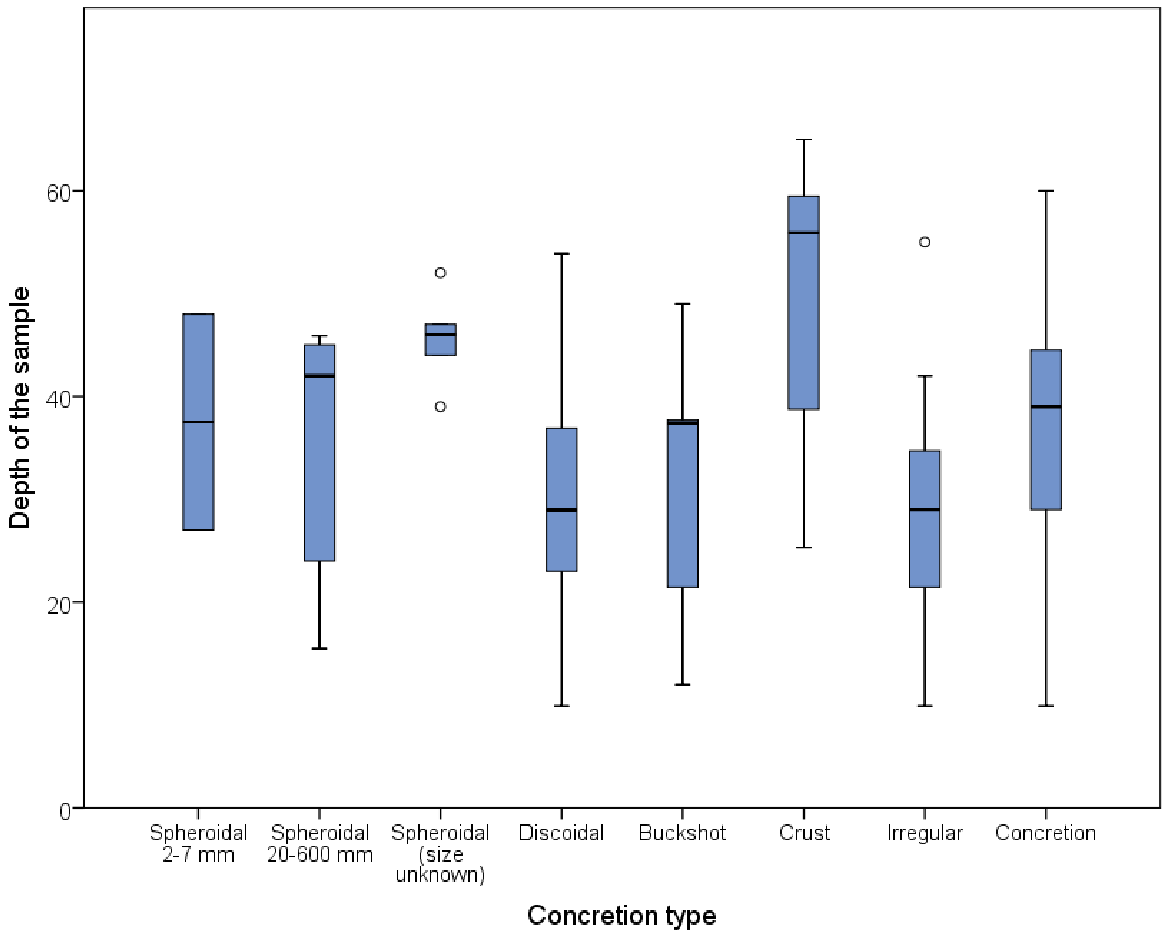

Figure 7. Water depth range of different concretion types. The box plot graph shows the distribution of each dataset; minimum values (excluding outliers) are shown by the lower lines extending from the boxes (first quartile), median is shown as the horizontal line in the box and the upper lines represent the maximum values (excluding outliers) and the upper quartile of the dataset. Small circles are outliers that represent extreme values of the dataset.

Table 5. Sediments associated with spheroidal concretions: sediments above the concretions, sediments below the concretions/the sediments where the concretions were found and the sediment on the bottom of the sample.

Sediments	**Sediments on top of the concretions**			**Sediments below the concretions**			**Bottom sediments**		
	Spheroidal 2-7 mm	Spheroidal 20-600 mm	Spheroidal (size unknown)	Spheroidal 2-7 mm	Spheroidal 20-600 mm	Spheroidal (size unknown)	Spheroidal 2-7 mm	Spheroidal 20-600 mm	Spheroidal (size unknown)
Clay					30%			22,2%	14,3%
Varved clay					20%	28,6%	50%	55,6%	57,1%
Sulphide clay					10%			11,1%	
Silty clay							50%		14,3%
Muddy clay				50%					14,3%
Mud						14,3%			
Sand				50%	30%	42,9%		11,1%	
Silty sand									
Muddy sand		10%			10%				
Clayey sand						14,3%			
No sediment	100%	90%	100%						
Number of samples	2	10	7						

5.2.2 Discoidal and crust concretions

Discoidal and especially crust concretions were occasionally found widely distributed on the bottom of the sea which is common in the GOF. In some sampling sites crust concretions formed a wide and thick layer as seen in Figure 3D. Both discoidal and crust concretions were quite large in size, up to 8 cm and 7 cm in diameter (respectively).

The sediments associated with discoidal concretions had the widest variability as seen in Table 6 and Figure 8. The thin sediment layer above the concretions reflects the underlying sediments; both were mostly muddy sand or sand in roughly half of the samples. Discoidal concretions were most frequently found on sand or sandy sediments whereas all other concretions types were most commonly found underlain by clay or clayey sediments. In some samples the sediments underlying discoidal concretions were represented by finer sediments such as clay and coarser sediments e.g. stony sand and glacial till. The bottom sediments were mostly clay. The seabed structure was most commonly crest which is reflected by the sandy sediments associated with these concretions.

Majority of the crust concretions were found on clay, muddy sand or other fine grained sediments such as silty mud. The bottom sediments were mostly clay or clayey sediments. Figure 3D shows the crust concretions on the seafloor and the same concretions are seen in Figure 1D. The seabed structure was either crest or low relief seabed structure i.e. basin or plain.

5.2.3 Irregular concretions

Irregular concretions consist of concretions that did not fit any other category. In this study they are not considered as a concretion type, rather a group of samples with irregular morphology. These concretions were generally found relatively shallow. Most common seabed structure was crest however they were found also on basins and valley and troughs. Slope and roughness values were similar than with discoidal concretions. Table 7 shows that the topmost sediment was sand, muddy sand or clayey sand. These concretions were found on top of the uppermost sediment layer i.e. they were not embedded in the sediment column. Sediments below the concretions were mostly clay or sandy sediments. Bottom sediments were clay in majority of the samples.

5.2.4 Concretions

These concretions are found at depths of 9,9m to 60 m and on all seabed structure types of which crest is most common. The sediments associated with these concretions vary significantly which is probably due to the fact that these samples may cover all concretion types. Sediments on top were most commonly sandy sediments. Sediments below the concretions ranged from clay to stones, clay and sand being the most common sediments. Bottom sediments were commonly clay or clayey sediments.

5.2.5 Samples with several concretion types

There were 16 samples that had two or more concretion types in the same sampling site. All concretion types were found to co-exist with at least one other concretion type of which discoidal concretions were the most common. Majority of these samples were found on crests. All other concretions types apart from crust concretions were found at deeper water depths when associated with another concretion type. Buckshot concretions were found up to 14,4 m deeper than samples that had only buckshot concretions in the sampling site.

Table 6. Sediments associated with discoidal, buckshot and crust concretions: sediments above the concretions, sediments below the concretions/the sediments where the concretions were found and the sediment on the bottom of the sample.

Sediments	**Sediments on top of the concretions**			**Sediments below the concretions**			**Bottom sediments**		
	Discoidal	Buckshot	Crust	Discoidal	Buckshot	Crust	Discoidal	Buckshot	Crust
Clay				8,9%	28,5%	10%	20%	40%	
Varved clay				2,2%		30%	30%	20%	33,4%
Sulphide clay				2,2%			6,7%		11,1%
Silty clay							16,7%		22,2%
Muddy clay					14,3%				
Sandy clay	2,5%				14,3%	10%	3,3%	20%	
Mud	2,5%		9,1%	4,4%		10%			
Silty mud						10%			
Sandy mud	2,5%			6,7%			6,7%		
Silt		14,3%							
Sandy silt	2,5%			4,4%					
Sand	25%			22,2%	14,3%	10%	3,3%	20%	11,1%
Silty sand	2,5%			4,4%					
Muddy sand	27,5%	28,6%	27,3%	24,4%		20%			
Clayey sand	2,5%			8,9%	14,3%		6,7%		
Stony sand				8,9%			3,3%		
Stones			9,1%						
Glaciall till				2,2%			3,3%		22,2%
No sediment	32,5%	57,1%	54,5%						
Number of samples	41	7	11						

Table 7. Sediments associated with irregular concretions and concretions (no description): sediments above the concretions, sediments below the concretions/the sediments where the concretions were found and the sediment on the bottom.

	Sediments on top of the concretions		**Sediments below the concretions**		**Bottom sediments**	
	Irregular	Concretion	Irregular	Concretion	Irregular	Concretion
Clay			8,3%	30,8%	33,34%	58,1%
Varved clay			25%	3,2%	22,24%	9,1%
Sulphide clay				1,1%		3,5%
Silty clay					11,1%	4,7%
Muddy clay		3,3%	16,7%	9,5%		1,2%
Sandy clay					11,1%	
Sandy muddy clay				2,1%		
Sand	25%	5,4%	16,7%	29,7%	11,1%	8,1%
Silty sand				1,1%		1,2%
Muddy sand	16,7%	7,6%	16,7%	9,6%	11,1%	1,2%
Clayey sand	8,3%		8,3%			2,3%
Stony sand				4,3%		1,2%
Silt						4,7%
Clayey silt						3,5%
Sandy silt		1,1%		1,1%		
Mud			8,3%	3,2%		
Silty mud		3,3%		1,1%		
Sandy mud				1,1%		
Stones		1,1%		2,1%		
Glaciall till						1,2%
No sediment	50%	78,2%				
Number of samples	12	94				

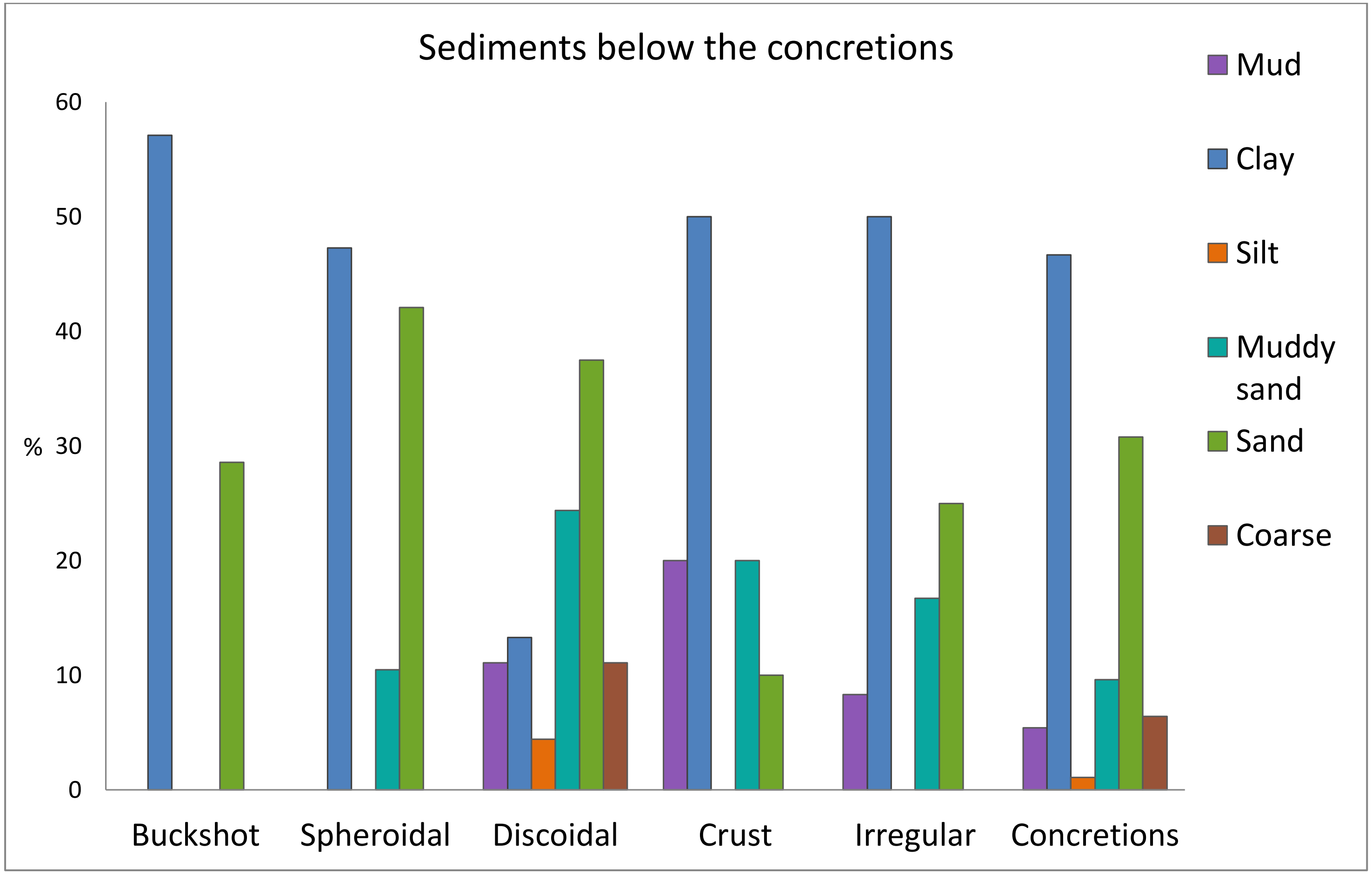

Figure 8. Sediments below the concretions. Mud includes: mud, silty mud and sandy mud,clay includes: clay, varved clay, suplhide clay, muddy clay, sandy clay and sandy mud clay, silt includes: silt, clayey silt and sandy silt, sand includes: sand, silty sand and clayey sand, coarse includes: stony sand and glaciall till.

5.3 Environmental variables

Environmental variables slope, roughness (20 km), surface wave exposure, bottom wave exposure, distance to coast and to river and bottom current velocity (m/s) of different concretion types are seen in Table 8.

5.3.1 Slope and roughness

Average slope values were highest with buckshot, crust and discoidal concretions. Discoidal concretions had the widest range in slope and roughness values and also the highest and lowest single values in both variables.

5.3.2 Distance to the coast and to river

The range in distance to the coast of spheroidal (not 2–7 mm), crust and irregular concretion types appears to be larger than that of the discoidal and buckshot concretions (Figure 11). Discoidal and buckshot concretions were generally found closest to coast. Discoidal and crust concretions had the widest range in distance to river. Concretions (with no description) and crusts covered a wide range in relation to both variables.

5.3.3 Surface wave exposure

Surface wave exposure (SWE) in relation to depth is illustrated in Figure 8. The SWE values increase as the depth increases. In the archipelago area near the coast and near e.g. islands the SWE values are lower.

5.3.4 Bottom wave exposure

The average bottom wave exposure (BWE) of discoidal concretions was several folds higher than that of other concretion types and had also the highest range as seen in Figure 9 and 10. Highest BWE values are found in crests whereas in the areas of basins, valley and troughs and plains the value stays fairly constant (Figure 10). Spheroidal concretions have the lowest average BWE values apart from bigger spheroidal concretions (20–600 mm) which had the second highest average BWE values.

5.3.5 Bottom current velocity (m/s)

The sampling sites of spheroidal concretions had the highest bottom current velocity (BC) values and also the highest range in these values. Highest average BC velocity value was found with the spheroidal concretions (size unknown). Crust concretions had also high BC velocity values whereas buckshot concretions were found in areas of low BC velocity values.

Figure 13 illustrates depth in relation to BC velocity. Crust concretions seem to form in certain BC velocity range and spheroidal concretions (size unknown) also show some dependency in BC velocity.

Table 8. Environmental variables of different concretion types (range and average values).

Concretion type	Slope (degree)	Roughness 20k	Surface wave exposure	Bottom wave exposure	Distance to coast (m)	Distance to river (m)	Bottom current velocity m/s
Buckshot	0,28 - 1,21 av.0,72	0,4 - 0,44 av.0,42	29877 - 432926 av.266880	61 - 5954 av.1881	250 - 4366 av.1876	18481 - 32249 av.22374	0,001 - 0,010 av.0,006
Spheroidal 2-7 mm	0,42 - 0,46 av.0,44	0,42 - 0,43 av.0,43	180546 - 429218 av. 304882	39 - 139 av.89	1904 - 3824 av.2864	18832 - 21866 av.20349	0,0036 - 0,0108 av.0,0118 m/s
Spheroidal 20-600 mm	0,19 - 0,97 av.0,51	0,42 - 0,47 av.0,43	164141 - 443337 av. 341460	29-25023 av.4475	1250 - 11411 av.5059	18028 - 33979 av.26510	0 - 0,0206 av.0,008
Spheroidal (size unknow)	0,22 - 0,61 av.0,44	0,42 - 0,44 av.0,43	424216 - 474075 av.446173	90 - 1688 av.573	2750 - 10983 av.6614	22060 - 3457 av.28668	0,01 - 0,02 av.0,0119
Spheroidal (all samples)	av.0,47	av.0,43	av.364273	av. 2560	av. 5182	av. 27295	av. 0,010
Discoidal	0,13 - 2 av.0,62	0,19 - 0,64 av.0,43	47505 - 446094 av. 269243	0,01-114525 av.11241	250,00 - 12966 av.2473	11051 - 42300 av.23150	0,0034 - 0,0208 av.0,0093 m/s
Crust	0,22 - 0,93 av.0,71	0,46 - 0,47 av. 0,47	462989 - 46865 av. 467589	0,17 - 13940 av.3588	1768 - 14769 av. 11950	14020 - 44931 av. 27755	0,0073 - 0,0117 av. 0,0108
Irregular	0,24 - 1,63 av.0,62	0,37 - 0,47 av.0,43	22760 - 446094 av.272437	0 - 28075 av.5300	250,00 - 9890 av.3064	18229 - 39425 av.25627	0,001 - 0,0110 av.0,0070

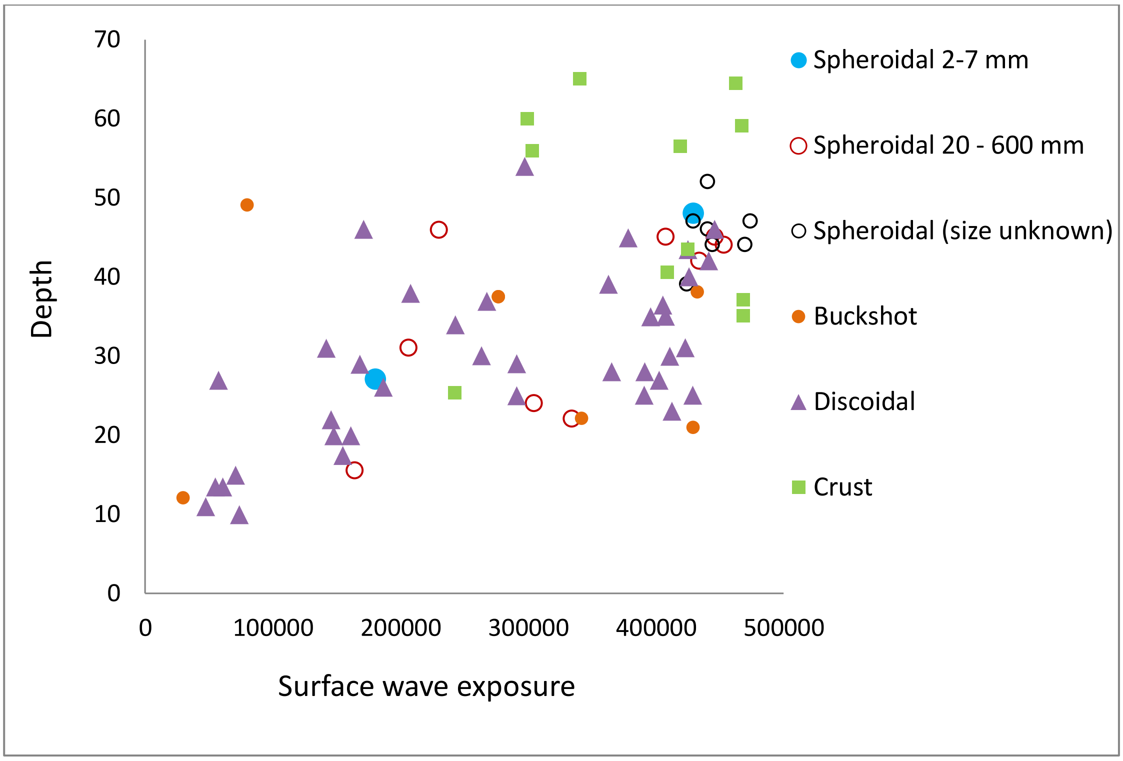

Figure 8. Surface wave exposure relative to water depth (m).

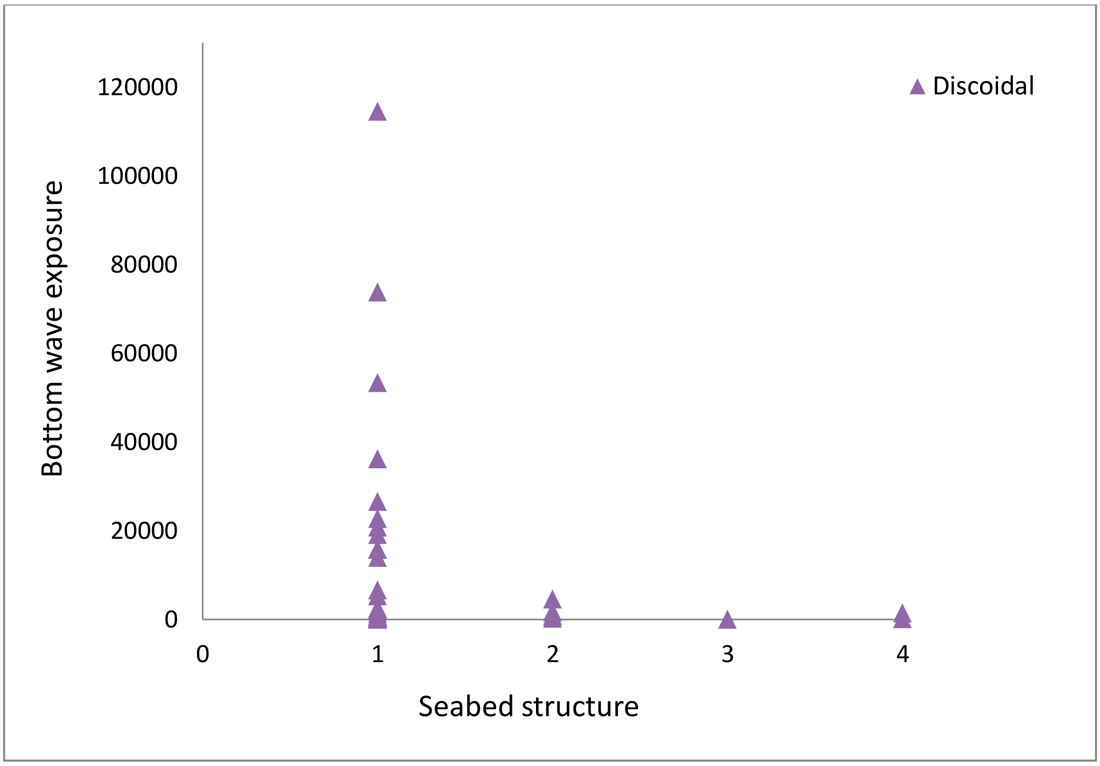

Figure 9. Seabed structure relative to bottom wave exposure at discoidal concretion sites. Seabed structures 1= crest, 2= basin, 3 = valley and trough and 4= plain.

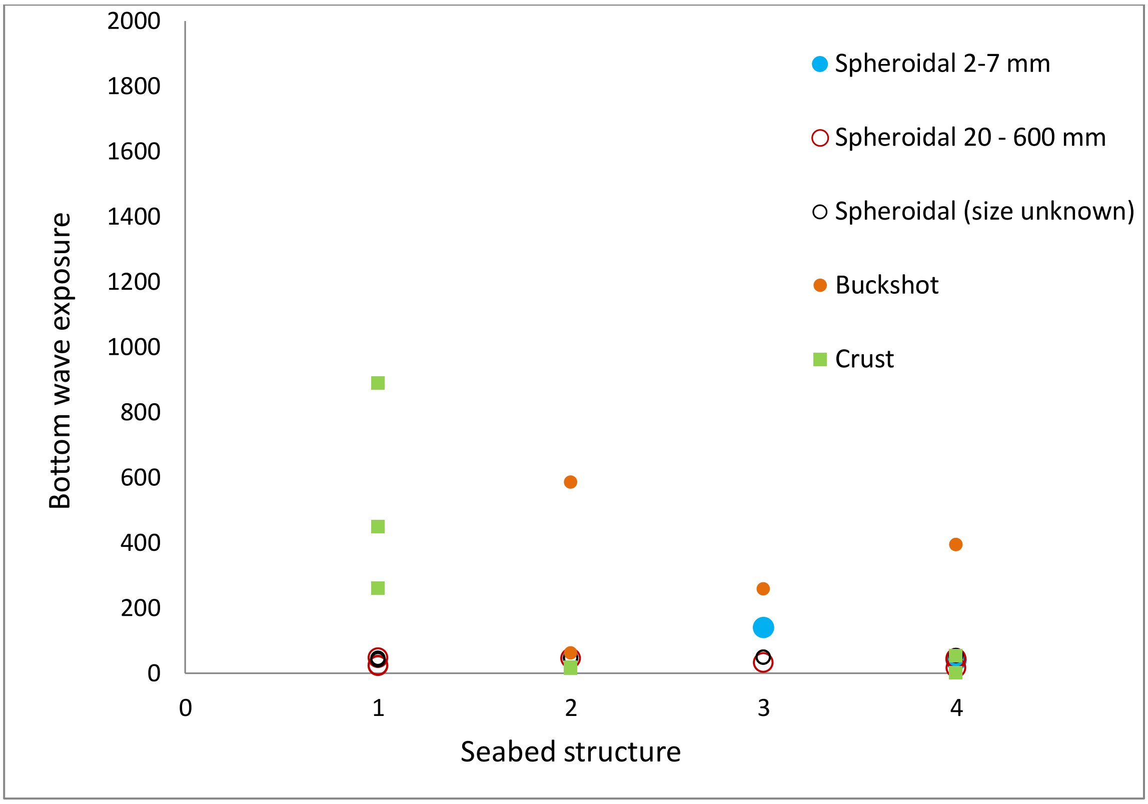

Figure 10. Seabed structure relative to bottom wave exposure at spheroidal, buckshot and crust concretion sites. Seabed structures 1= crest, 2= basin, 3 = valley and trough and 4= plain.

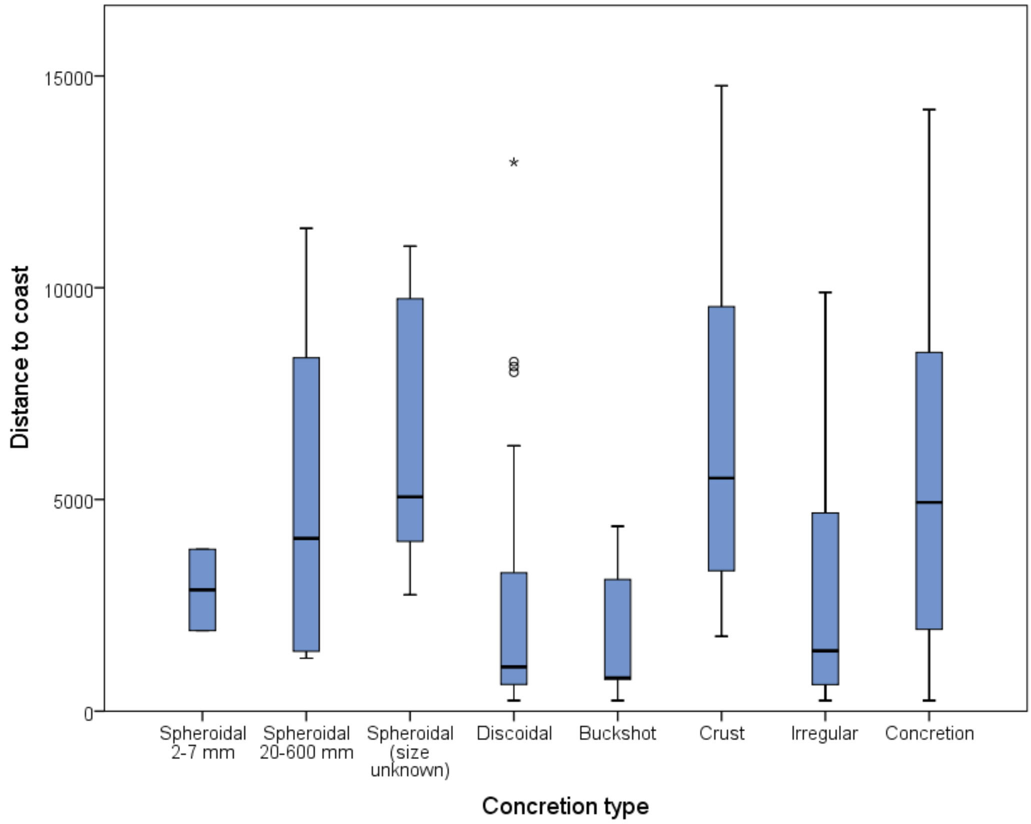

Figure 11. Distance (m) to coast of different concretion types.

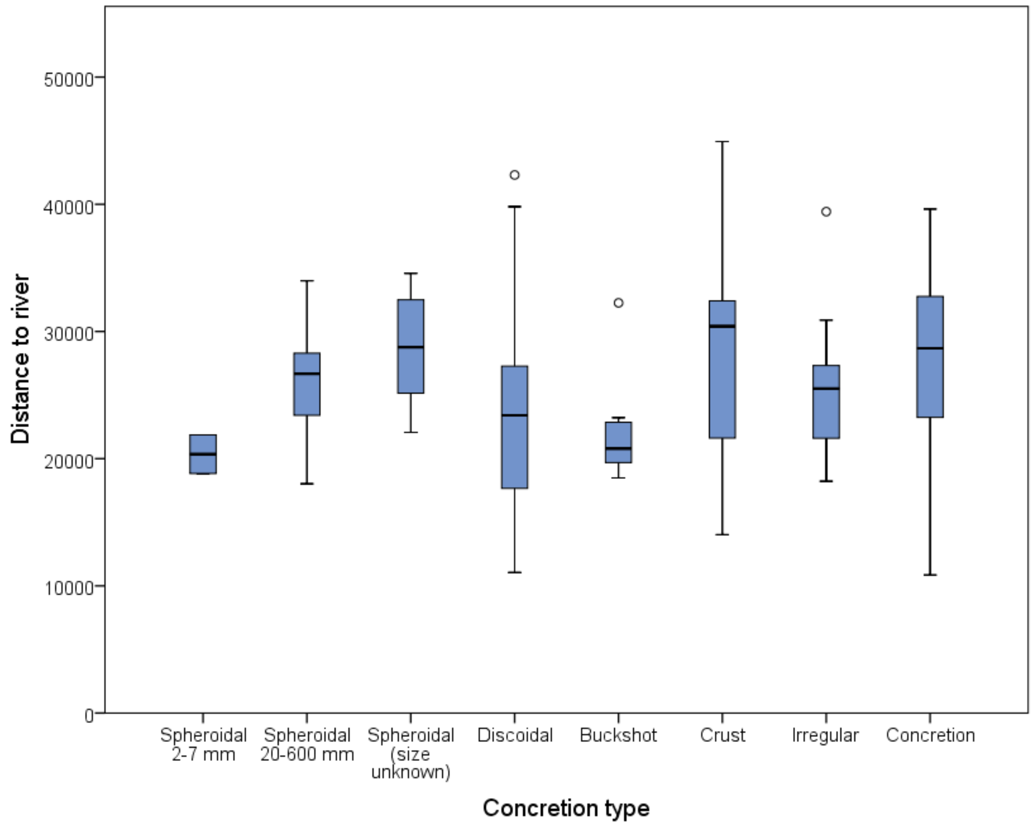

Figure 12.Distance (m) to river of different concretion types.

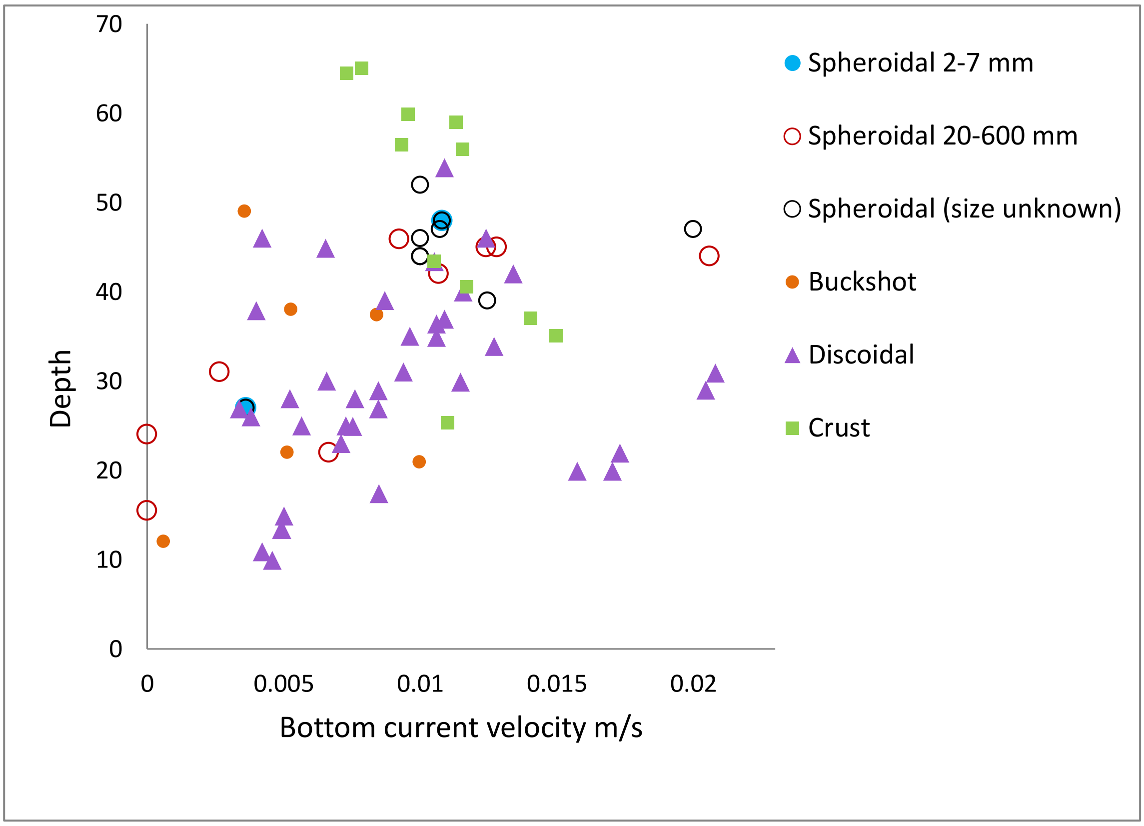

Figure 13. Bottom current velocity (m/s) relative to water depth (m).

6. DISCUSSION

6.1 Environmental variables

6.1.1 Sediments

Though the topmost sediment was missing in majority of the samples due to the sampling method, the videos confirmed that there was usually a thin sediment layer covering the concretions.

Clay was clearly the most common sediment type below majority of different concretion types followed by sand and muddy sand (Figure 8). Discoidal concretions were most commonly found on sand or muddy sand (Table 6) which is a common seabed substrate type associated with these concretions (Winterhalter 2004). These concretions were also most frequently found underlain by coarser substrates. The underlying sediments of discoidal concretions reflect the seabed structure type as crests are commonly features where sand, clay and coarser substrates are found (Kaskela et al. 2012). In some samples the samplers/corers used did not reach the bottom sediments due to coarser grained sediments such as glaciall till and/or the thickness of the sandy sediments. In some cases (Figure 14) these sandy sediments on the top of the sample are residual (due to erosion) sediments, which often cover the exposed glacial clays at the seabed (e.g. Kaskela et al. 2012).

Figure 14. Photo of seabed sediment sample showing that glacial clay is covered with a thin residual sediment (mainly sand and gravel). Photo: SGU.

6.1.2 Seabed structure, slope and roughness

The gradation of the seafloor from archipelago area to offshore is not smooth and especially in the northern GOF several different geomorphological seafloor types are found (Kaskela et al. 2012). Crests cover up to a third of the GOF seafloor and are more common in the northern areas rather than the central GOF (Kaskela et al. 2012) hence it is not surprising that crests were the most common seafloor structure type in the study area. The geodiversity of the BS area generally increases towards archipelago areas and from south to north (Kaskela and Kotilainen 2017). The distribution of different concretion types could illustrate this feature of the northern GOF with respect to environmental variables that are limiting factors in the formation of ferromanganese concretions such as the substrate type and the bottom currents. The morphology of the seafloor also impacts nutrient availability (e.g. phosphorous), pH and toxins (Lawler et al. 2015). Areas of high geodiversity i.e. high heterogeneity show positive correlation with high species richness (Stein et al. 2014, Kaskela and Kotilainen 2017) which could be linked to ferromanganese concretion formation.

Due to the broad resolution of the slope and roughness variables they provide more reliable results when used in a larger scale environment rather than in a small scale and complex local environment such as the archipelago areas (Kaskela and Kotilainen 2017). Areas of high slope and roughness values are often dynamic environments where deposition and erosion can vary within short distances. Though slope areas are rare in the BS area they are linked to high geodiversity which could be connected to the seafloor hydrodynamics e.g. the isolation from bottom currents (Kaskela and Kotilainen 2017). The slope values of buckshot concretions were among the highest which likely describe the heterogeneity of the local environment where also calmer areas are found and where the environmental conditions for the formation of buckshot concretions are plausible: low bottom currents and the availability of compositional material trough erosion and resuspension. With discoidal concretions the slope and roughness values were high which is consistent with the fact that they are commonly found on crests and in areas of high bottom currents (Table 8).

6.1.3 Distance to river and distance to coast

The distance to river is a variable describing the supply of fluvial material to the sea and small distance to the river might indicate the dependence in the availability of e.g. Fe (Kaskela and Kotilainen 2017). Flocculation of Fe and flocculation of dissolved organic matter has been identified as an important mechanism of Fe sedimentation in coastal areas by affecting the chemistry of sediments and the diagenetic reactions involving Fe. The flocculation of Fe occurs between the contact horizon of fresh and saline water masses leading to the accumulation of labile Fe in the form of ferrihydrite and Fe (III)-OM. Offshore the flocculation is likely dependent on the steepness of the salinity gradient. The flocculated iron is transported to bathymetric depressions by currents and redox shuttling (Jilbert et. al. 2018). This mechanism is likely to be the source of Fe of concretions in the coastal areas. The GOF is a small-scale basin compared to the larger oceans and the sampling locations were all relatively close to coast and to rivers. Though the results show that some discoidal concretions were found closer to river than other concretions types, the range was also high (Table 8, Figure 11). Nevertheless the differences in the results in this respect are clearer among discoidal concretions. Also buckshot concretions seem to form in a certain range in relation to distance to river however the number of samples is so low that it is unreliable to make conclusions on this basis.

The coastal areas of the GOF are active and fragmented seafloor environments where various processes modify the seafloor (Kaskela et al. 2012, Kaskela and Kotilainen 2017). Distance to coast gives insight how sensitive the concretions are to these processes and it could also be connected to the source of the compositional materials and processes related to it. Crust concretions and spheroidal concretions (size unknown) were found furthest away from the shore (Table 8, Figure 11). Crusts were found in relatively high-energy environments as the BWE and BC velocity values were quite high and based on previous studies (Winterhalter 1966), they possibly withstand the fluctuating environments of the coastal areas. The reason why they are not common in the coastal areas is possibly due to the water depth, quality of the seabed and the source of Fe and Mn.

6.1.4 Wave exposure

SWE values as assumed showed smaller values in the sheltered archipelago areas and increasing values at higher water depths (towards open ocean) (Figure 8). Typically the BWE values were highest in areas where the seabed structure was crest and lower values were found in areas of valley and troughs, plains and basins. This is because the areas of crests are elevated features and more open and therefor the bottom wave impact is higher.

6.1.5 Bottom current velocity (m/s)

The results showed that there is variance in the BC velocity values among different concretion types (Table 8). The BC velocity was high in areas of spheroidal concretions which is a commonly known feature in the area of their formation (Glasby et al. 1997) and also in areas where crust and discoidal concretions were found which is consistent with previous studies (Winterhalter 1966). Buckshot concretions were found in areas of low BC velocities which was expected as they are commonly found in fine grained sediments.

6.2 Spheroidal concretions

Spheroidal concretions were categorized into groups by size. Small spheroidal concretions (2–7mm) were so few in number that it is not reliable to make any conclusions with this group. The only clear observation is that bigger spheroidal concretions with a size range of 20–600 mm are more abundant in the study area (Table 4). However the sizes of some spheroidal concretions were unknown (7 samples) and therefore reliable conclusions about the distribution of different sized spheroidal concretions in the study area cannot be made. Spheroidal concretions with a size range of 20–600 mm had the highest number of samples and this is why the focus is on this group. These concretions are most likely transient or irregular spheroidal/ellipsoidal forms as in the Zhamoida (2004) classification. Furthermore these concretions had similar results with concretions in the irregular concretion group which indicates that they are formed in similar environments. Spheroidal concretions (2–7 mm) and spheroidal concretions with no information about their size had also similar results (slope, roughness, BWE, BC velocity and distance to river) which could indicate that at they are possibly similar concretion formations (Table 8).

Usually spheroidal concretions are found in areas of high bottom current velocities (Glasby et al 1997). The BC velocity values of all spheroidal concretions (average of all samples) were high and they were also among the highest comparing to other concretion types which is consistent with previous studies (Table 8). The average BC velocities of spheroidal concretions with a size range of 20–600 mm were clearly lower than the average of other spheroidal concretions, crust and discoidal concretions. These concretions were also found in areas of both low and high BC velocities (0–0.0206 m/s) indicating that the BC velocity might not be a limiting factor in their formation. The average BWE values were among the highest of all concretion types (Table 8). They were found most commonly (comparing to other spheroidal concretions) on crests which are not typical environments for spheroidal concretions (Table 4). Also the slope values were higher than with other spheroidal concretions though not reaching the corresponding values of buckshot, crust and discoidal concretions. They were not found as close to coast as discoidal and buckshot concretions and the range in distance to coast was wider. Though the sampling locations were mostly concentrated offshore as opposed to near the shoreline it seems that these concretions form in areas that are not in the proximity of the coastline.

Spheroidal concretions with a size range of 2–7 mm were not abundant in the study area. These concretions are usually found on edges of basins (Zhamoida 1996) which are more common in the central and eastern GOF (Kaskela and Kotilainen 2017). Though basins and plains covered roughly one third of the study area these concretions were practically missing in the study area. It is possible that these concretions are more abundant in the deeper areas of the central GOF and therefore they were not found in the sampling sites of this study. As the seabed structures of the eastern GOF are characterized by basins and plains and the northern GOF is characterized by a combination of several seafloor structure types (Kaskela et al. 2012) it is not surprising that spheroidal concretions are not as abundant in the northern areas as in the eastern GOF. Also the highest manganese concentrations have been found in the deepest concretion fields where the manganese mobilization and migration in the anoxic environment is more active (Zhamoida et al. 1996). Though spheroidal concretions have been found in both shallow and deeper water depths (Zhamoida 2004) ultimately the availability of Mn and Fe is the most important factor controlling the formation of spheroidal concretions (Zhamoida et al. 1996).

6.3 Buckshot concretions

The small number of samples makes the interpretation of the environments where buckshot concretions are formed quite difficult. Buckshot concretions were found on all bottom structure types and on both shallow and deeper areas (Figure 7, Table 4). It seems that these concretions prefer calm conditions: BC velocity and BWE were low indicating low-energy environments. Furthermore the sediments on top and below buckshot concretions were usually fine grained sediments which are commonly found in areas of low bottom currents.

These concretions were also found closer to coast on average comparing to the majority of other concretion types (Table 8, Figure 11). This can also be seen in the maps showing the sampling sites (Figures 4-6). The distance to coast does not correlate with water depth and although coastal areas are commonly high energy environments the buckshot concretions are possibly found in sheltered archipelago areas or deep enough in the coastal areas so that the coastal processes do not have major influence in the area of their formation. As mentioned before the slope values of buckshot concretions were high which also point towards the heterogeneity and sheltering character of the local environment. Also the distance to river was clearly narrower with buckshot concretions when comparing to the other concretion types indicating some dependency to the proximity to rivers. Considering all the results it seems that the buckshot concretions favor environments where the seabed substrates are fine grained sediments, calm conditions and possibly proximity to the coast. The number of samples was low and more reliable results could be obtained with larger sample number.

6.4 Discoidal concretions

Majority of discoidal concretions were found on crests which are commonly found in areas of crystalline rock basement. The slope and roughness are indirect variables that reflect processes such as material flow and currents (Grohmann et al. 2011 and Kaskela et al. 2017) though these variables reflect the structural aspects of the bedrock which in turn reflects the pre-glacial and glacial processes rather than the modern environment (Kaskela and Kotilainen 2017). Modern environments with high slope and roughness values correlate with the crystalline rocks and these areas are often dynamic environments where the deposition and erosion can vary within short distances (Kaskela and Kotilainen 2017). The results also indicate towards this since crests were found to be areas of dynamic environments. The BC velocity values were high on average though the range was also high and therefor the formation of discoidal concretions is possibly not dependent on high bottom currents only.

Discoidal concretions are found closer to coast compared to e.g. crust concretions (Table 8, Figure 11). This may be because these concretions are common in crests which are found both near the shore and offshore. However the discoidal concretions are found in archipelago areas that are not sheltered and therefore is seems that they are not as sensitive to the effects of the coastal processes. The BWE values of discoidal concretions are several folds higher than with other concretion types which is consistent with the fact that they are common in elevated surfaces that are more open and susceptible to processes affecting on the seafloor. The distance to river has a wide range indicating that discoidal concretions might not be as dependent on the river supply of Fe to the GOF. In the coastal areas the availability of Fe could also be linked to erosion and resuspension of Fe-bearing materials. Altogether discoidal concretions seem to withstand fluctuations in the environment such as bottom currents and near shore processes and are not sensitive to high-energy environments. This might also explain why discoidal concretions are the most common concretion type in the study area.

6.5 Crust concretions

Crust concretions were found deeper than any other concretion type (25,3–65 m), they were commonly found on crests and also on low relief seafloor structure types (Table 4) and the underlying sediments associated with these concretions were most commonly clay or sandy sediments (Table 6) which are consistent with previous studies in the BS area (Winterhalter 1966, 2004).

BC velocity was high which is supported by the fact that crusts usually form in areas of low sedimentation rates. These concretions also seem to form in certain bottom current velocity range as seen in Figure 13. Winterhalter (1966) suggests that crust concretions can be broken down to smaller pieces and accumulate together as a result of dissolution or e.g strong bottom currents i.e the conditions in the areas of crusts are not calm. The average BWE values were only higher than with spheroidal concretions (2–7 mm and size unknown) and buckshot concretions which indicate that crusts form in areas that are somewhat sheltered from the wind induced wave exposure (Table 8). Nevertheless the BWE values of crusts were over twice as high as with buckshot concretions. The BWE values are likely linked to the high slope and roughness values indicating that the environments where crust concretions were found are not as exposed as with discoidal concretions and then again in areas where the high bottom currents can reach the concretions i.e the environment is heterogenic. Variables that may be determining factors in the formation of crusts could be the BC velocity which was clearly high on average. None of the samples were found in areas where BC velocity was close to zero as opposed to other concretion types and also the fact that crusts formed in a certain BC velocity range could be significant. Other factors controlling their formation are possibly the underlying sediments which were commonly clay or sandy sediments and the water depth which was quite deep.

These results show that there are some notable differences in the environments where crust and discoidal concretions form. Especially the BWE values, water depths and distance to coast differ significantly. On the contrary the seafloor structure types, relatively high BC velocities and distance to river indicate towards similar environments.

6.6 Irregular concretions

These concretions are possibly transient or relict forms. The results of these concretions resemble the ones of spheroidal concretions (20–600 mm); slope, roughness, BWE, distance to river and BC velocity (Table 8) and the sediments associated with these concretions are somewhat similar (Table 5, Table 7). There were some differences in the distance to coast and in the depth ranges however the difference was not strikingly different. The factors that may have influenced the formation of these concretions could be changes in the environmental conditions such as changes in the sedimentary environment e.g. burial of the concretions or anoxia (Zhamoida et al. 2007). These concretions were also found at deeper water depths where the seasonal anoxia below the halocline is not uncommon (Vallius et al. 2011) hence the occurrence of these concretions could indicate towards anoxia in the local environment.

6.7 Concretions with no description

When looking at the samples with no description (concretions) most concretions are found in areas where the sediment type is clay or sand and the seabed structure is crest.

The depth varies from 9,9 m to 60 m. Based on these observations it is likely that the concretions with no description cover most likely all concretion types. Based on the fact that half of all the samples were found on crests and that discoidal concretions were the most common concretion type found on crests, it is likely that discoidal concretion is the most common concretion type or at least abundant concretion type in this group

6.8 Samples with several concretion types

Some samples (8% of all samples) had more than one concretion type in the sampling site. Concretions in these samples were found deeper than when not associated with another concretion type. This is possibly linked to the availability of Mn which as mentioned before increases as depth increases. Also at deeper water depths the environment is possibly calmer and suitable for various concretion types.

7. CONCLUSIONS

The samples of this study covered sea areas in the northern GOF mainly from Kirkkonummi to Virolahti. The main focus of this study was to classify the concretions into different concretion types, illustrate the distribution of the different concretion types in the sampling area and to investigate how the environmental variables affect the formation of these concretions. Previous studies concerning the environments of ferromanganese concretions and the results of this study show similar results. The sediments and seabed structures associated with ferromanganese concretions and the bottom currents are all known factors that influence the formation of the concretions. Here the environmental variables used showed differences in the environments where each ferromanganese concretion type is formed. New information was obtained with the variables slope, roughness, wave exposure and distance to coast and distance to river and more accurate information was obtained with the variable bottom current velocity (m/s). The differences in environments associated with each concretion type are most reliably evaluated when the environmental variables are interpreted together. Oxygen conditions of the local environment is an important factor in the formation of ferromanganese concretions however detailed data of the oxygen concentration in the study area was not available at the time of this study. Most reliable results were obtained with discoidal concretion type simply because of the high number of samples. Especially spheroidal concretions (2–7 mm and size unknown) and buckshot concretions had a low number of samples which indicates that they are not common in the study area.

The results showed that spheroidal concretions (2–7 mm) were not common in the study area which is possibly linked to the quality of the seabed and the availability of Mn and Fe in the study area. Spheroidal concretions with a size range of 20–600 mm had similar results as irregular concretions. It is likely that these concretions represent the transient and/or irregular ellipsoidal concretion type. Though the number of buckshot concretions was small in the study area it its quite clear that these concretions form in calm environments. The areas are characterized by low bottom current velocity, low bottom wave exposure values and fine grained sediments. The environments where discoidal concretions were found were commonly dynamic and high energy environments based on the high bottom currents, high bottom wave exposure values and high occurrence of these concretions in crests. When considering the study environment as a whole, the area is most likely the most favorable for the formation of discoidal concretions. Crusts were found quite deep and in areas of high bottom currents. Factors that most likely have influence on the formation of crusts are the water depth, underlying sediments and (high) bottom currents in the areas of crusts.

The abundance of ferromanganese concretions in the GOF area is high and the economic interest towards these concretions is likely to grow in the future. The significance of ferromanganese concretions to the local ecosystem is not yet fully understood. The ferromanganese concretions were listed in the second assessment of threatened habitat types in Finland Data Deficient which shows that the knowledge of this marine habitat type is still incomplete.

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